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CONTENTS

SECTION A.—PHYSICAL SCIENCES

	Page
Resonance Method for Measuring the Ratio of the Specific Heats of a Gas, C_p/C_v . Part I— <i>A. L. Clark and L. Katz</i> -	22

SECTION B.—CHEMICAL SCIENCES

The Equilibrium Pressures of Oxygen Adsorbed on Activated Charcoal— <i>M. J. Marshall and R. A. Findlay</i> - - - -	35
The Quenching of Mercury Resonance Radiation by Ethylene— <i>E. W. R. Steacie</i> - - - - -	44
Cadmium Photosensitized Reactions of Ethylene— <i>E. W. R. Steacie and R. Polvin</i> - - - - -	47
The Density of Gaseous Chlorine— <i>A. S. Ross and O. Maass</i> -	55
Solid Solutions of Hydrogen Peroxide and Water— <i>P. A. Giguère and O. Maass</i> - - - - -	66

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NUMBER 2

RESONANCE METHOD FOR MEASURING THE RATIO OF THE SPECIFIC HEATS OF A GAS, C_p/C_v ¹

PART I

By A. L. CLARK² AND L. KATZ³

Abstract

This paper contains the description with theory of a modification of Assmann's method for determining $\gamma = \frac{C_p}{C_v}$, the ratio of the specific heats of a gas. The gas is enclosed in two chambers formed by the ends of a cylinder and a steel piston in the middle of the cylinder. This piston is caused to oscillate by an alternating current applied in coils outside the cylinder, thus subjecting the gas to alternate compression and rarefaction. The system has a natural frequency depending on the constants of the apparatus and the value of γ peculiar to the gas. The frequency of the a-c. current is varied, the amplitude of the motion of the piston observed, and the frequency for resonance measured. From this frequency and the constants of the apparatus the value of γ is determined. The method yields results of great accuracy and reproducibility.

The ratio of the specific heats of gases, $\gamma = C_p/C_v$, is a quantity of such importance both theoretically and practically that many observers by a variety of methods have measured its value for the common gases. All methods so far devised for the direct* measurement of γ depend essentially on taking the gas through one or more adiabatic cycles (or a fraction of a cycle) and observing associated phenomena, such as the change in pressure (method of Clément and Désormes†), change in temperature and pressure (method of Lummer and Pringsheim†), ratio of the adiabatic pressure change to the isothermal pressure change (method of Maneuvrier†), or the reaction of the gas to compression, involving the adiabatic elasticity $(\partial P/\partial v)_Q$ of the gas (method of Assmann† with low frequencies, and velocity of sound method with high frequencies). The main distinguishing features of these various methods are the rate at which the cycles occur and the associated phenomena observed.

The resonance method developed by the authors falls in the last-mentioned class, being dependent upon the adiabatic elasticity of the gas. It is an

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* Direct as compared to the more indirect method of measuring experimentally or calculating from spectroscopic data C_p and C_v separately and taking their ratio.

† A complete summary of all the important works prior to 1924 may be found in Reference (16).

adaptation of Assmann's method, and, while there have been modifications of the method by other investigators, it is little known and will therefore be described briefly. The gas to be investigated was enclosed by Assmann in the sealed ends of a U-tube filled with mercury. He caused the mercury to oscillate, thereby subjecting the gas to alternate compressions and rarefactions. Assuming these changes to take place adiabatically, Assmann was able to calculate γ from the period of oscillation. The results obtained were in error since under the conditions of his experiments the compressions and rarefactions were not adiabatic.

Müller and later Hartmann† attempted to improve Assmann's method but met with little success. Hartmann pointed out the serious error in the results when the friction between the mercury and the walls of the U-tube is neglected.

More recently Rüchardt (18) developed a modified form of Assmann's method. He employed a glass bottle fitted with an air-tight stopper through which passed a vertical glass tube of uniform bore. An accurately fitted steel ball was dropped into the tube and γ calculated, as in Assmann's case, from the period of oscillation. Rinkel (17), using the same apparatus, claimed to have obtained better results by measuring the distance of the initial drop of the ball rather than the period of oscillation. Further work by Brodersen (1) with a photographic recording apparatus, gave values of γ for air, agreeing fairly well with the accepted value.

The methods of Clément and Désormes, and of Lummer and Pringsheim, take the gas through a fraction of a slow adiabatic cycle (an expansion or compression). In Assmann's method the cycles occur at the rate of one to three per second and in the velocity-of-sound method they occur at the rate of many hundreds of cycles per second or very much higher for the ultrasonic region. The work described in this paper is within a region of frequencies not previously employed (25 to 150 cycles per sec.). In some respects the method is similar to that of Assmann, but greatly reduces the adiabatic correction because of the higher frequencies used, and eliminates the uncertainty in his friction correction by establishing resonance rather than by measuring a decaying oscillation.

Briefly, the method is as follows. The gas under investigation is enclosed in two similar chambers (see Fig. 1) separated by a freely moving, close fitting steel piston.* An externally applied magnetic field causes the piston to oscillate back and forth, subjecting the gas volumes to alternate compressions and rarefactions. The reaction of the gas to the motion of the piston is analogous to that of two springs whose natural period may be measured by changing the frequency of the external magnetic field until resonance is obtained. γ is readily calculated from this frequency, the pressure, and the constants of the apparatus.

† A complete summary of all the important works prior to 1924 may be found in Reference (16).

* The complete unit composed of the gas container, cylinder, and piston will be called the resonator.

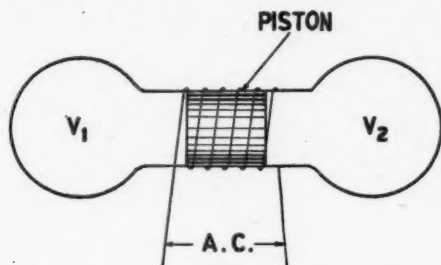


FIG. 1. Simple diagrammatic sketch of apparatus.

Mathematical Treatment

Equation of Motion

The piston is made to oscillate by passing an alternating current through the actuating coils. The lift magnet serves to counterbalance the weight of the piston and cuts down the friction to a very small value.

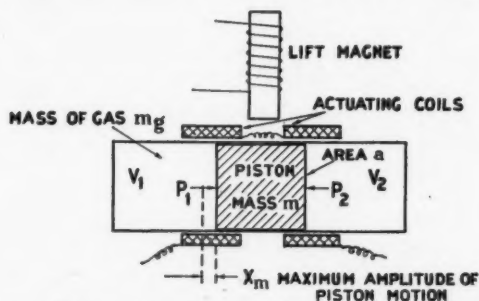


FIG. 2. Diagram showing dynamics of system.

If x is the displacement of the piston from its position of equilibrium at any instant,

$$(m + m_g)\ddot{x} + \beta\dot{x} + (P_2 - P_1)a = K \sin(\omega t - \varphi), \quad (1)$$

where

m = mass of piston,

m_g = effective mass of gas (mass of gas in one volume),

P_1 and P_2 are the instantaneous pressures acting on opposite sides of the piston,

a = area of piston,

β = friction factor,

$K \sin(\omega t - \varphi)$ = driving force due to magnetic field of actuating coils.

φ is introduced so that the motion of the piston may be written

$$x = x_m \sin \omega t. \quad (2)$$

It is shown further on that $(P_2 - P_1)$ may be separated into two components if the compressions are not strictly adiabatic, one in phase with the displace-

ment x and the other in phase with the velocity \dot{x} (see Equation (21)). Thus we may write

$$(P_2 - P_1) = (\Delta P)_x + (\Delta P)_\dot{x}. \quad (3)$$

Substituting in (1) we get

$$\ddot{x} + \beta' \dot{x} + \omega_n^2 x = K' \sin(\omega t - \varphi), \quad (4)$$

where

$$\begin{aligned} \beta' &= \frac{\beta + (\Delta P)_\dot{x}}{m + m_g} \\ \omega_n^2 &= \frac{a(\Delta P)_x}{x(m + m_g)} \\ K' &= \frac{K}{m + m_g}. \end{aligned} \quad (5)$$

Solving (4) gives

$$x = x_m \sin \omega t = \frac{K'}{\sqrt{(\omega_n^2 - \omega^2)^2 + \beta'^2 \omega^2}} \sin \omega t. \quad (6)$$

Differentiating (6) and equating to zero we get ω at the maximum amplitude

$$\omega_m^2 = \omega_n^2 - \frac{\beta'^2}{2} = \frac{a(\Delta P)_x}{x(m + m_g)} - \frac{\beta'^2}{2}. \quad (7)$$

It will be shown that $(\Delta P)_x$ involves the ratio of the specific heats of the gas γ . Solving gives the desired equation for γ in terms of ω_m^2 , β' , and the constants of the apparatus.

Solution for $(P_2 - P_1)$

As the piston oscillates, the gas in the two volumes is alternately compressed and rarefied. The resulting differences in the pressures in the two volumes, with volume and temperature as the independent variables, are given by an expansion according to Taylor's series.

$$\left. \begin{aligned} P_1 &= P_o + \left(\frac{\partial P}{\partial T}\right)_v \Delta T_1 + \left(\frac{\partial P}{\partial v}\right)_T \Delta v_1 + + \dots \\ P_2 &= P_o + \left(\frac{\partial P}{\partial T}\right)_v \Delta T_2 + \left(\frac{\partial P}{\partial v}\right)_T \Delta v_2 + + \dots \end{aligned} \right\} \quad (8)$$

giving

$$(P_2 - P_1) = \Delta P = \left(\frac{\partial P}{\partial T}\right)_v \Delta T + \left(\frac{\partial P}{\partial v}\right)_T \Delta v + +, \quad (9)$$

where

$$\Delta T = (T_2 - T_1), \quad \Delta v = (v_2 - v_1).$$

If the oscillations are small, we may write

$$\Delta P = \left(\frac{\partial P}{\partial T}\right)_v \Delta T + \left(\frac{\partial P}{\partial v}\right)_T \Delta v. \quad (10)$$

In general we must consider T , P , and v as functions of the co-ordinates as well as of time. Thus at any instant they may have different values at different points throughout the gas volume. For purely adiabatic changes,

the temperature of the gas would be a function of the time only (rising and falling in phase with the displacement of the piston), but since heat is lost by conduction to the walls the actual changes are not quite adiabatic. Consequently there is a temperature gradient toward the walls and therefore the temperature is a function of position as well as of time. For the same reason, the density of the gas ($\rho = 1/v$) is also a function of position as well as of time, and by Equation (10) we see that ΔP is no longer in phase with the piston displacement, but has a component in phase with the velocity.*

Thus in order to find $(P_2 - P_1)$ we need to take the mean integrated value of (10) over the whole volume where

$$\Delta \bar{P} = \left(\frac{\partial \bar{P}}{\partial T} \right)_v \Delta \bar{T} + \left(\frac{\partial \bar{P}}{\partial v} \right)_T \Delta \bar{v}, \quad (11)$$

where \bar{T} , \bar{P} , and \bar{v} are the average values taken over the whole volume at any instant, and are functions of the time only.

Solution for $\Delta \bar{v}$

If V_0 is the total volume of the gas on either side of the piston when it is at rest, and V_1 and V_2 are the volumes when it has suffered a displacement x , then by definition

$$\bar{v} = \frac{V}{m_g} \quad (12)$$

and

$$\left. \begin{aligned} \bar{v}_1 &= \frac{V_0 + ax}{m_g} = v_0 \left(1 + \frac{ax}{V_0} \right) \\ \bar{v}_2 &= \frac{V_0 - ax}{m_g} = v_0 \left(1 - \frac{ax}{V_0} \right) \end{aligned} \right\} \quad (13)$$

where a is the area of the piston end.

This gives

$$\Delta \bar{v} = (\bar{v}_2 - \bar{v}_1) = -2v_0 \frac{ax}{V_0}. \quad (14)$$

Solution for $\Delta \bar{T}$, Adiabatic Case

For strictly adiabatic compressions $\Delta \bar{T}$ is readily obtained as follows. From the first and second laws of thermodynamics we have the well known equations

$$dQ = C_v dT + T \left(\frac{\partial P}{\partial T} \right)_v dv \quad (15)$$

and

$$C_p - C_v = T \left(\frac{\partial P}{\partial T} \right)_v \left(\frac{\partial v}{\partial T} \right)_p. \quad (16)$$

* A component of ΔP in phase with the velocity would appear (Equation (5)) as an apparent increase in the friction of the moving system. Such an increase was actually observed. More power was required to oscillate the piston with the same amplitude when acting on gases of high conductivity than on those of low conductivity. For example, it took five times as much current in the actuating coils to cause the piston to oscillate with the same amplitude for He as for N₂.

The χ factor listed in Table II, etc., is a good indication of this effect.

Combining these equations and putting $dQ = 0$ for an adiabatic transformation,

$$\Delta \bar{T} = -(\gamma - 1) \left(\frac{\partial \bar{T}}{\partial v} \right)_P \Delta \bar{v}. \quad (17)$$

Substituting into Equation (11) gives*

$$\Delta \bar{P} = \gamma \left(\frac{\partial \bar{P}}{\partial v} \right)_T \Delta v = -2\gamma v_o \left(\frac{\partial \bar{P}}{\partial v} \right)_T \frac{ax}{V_o}, \quad (18)$$

which is the desired equation for $\Delta \bar{P}$ in terms of the piston displacement x .

$\Delta \bar{T}$ for Non-adiabatic Compressions

Since the actual compressions of the gas are not strictly adiabatic, a somewhat different treatment must be followed. This more involved deduction is given in Appendix I, where it is shown that

$$\Delta \bar{T} = 2(\gamma - 1) v_o \left(\frac{\partial \bar{T}}{\partial v} \right)_P \frac{a}{V_o} \left[\left(1 - \frac{3}{2n} \right) x - \frac{3}{2\omega_m n^2} (1 - n) \dot{x} \right], \quad (19)$$

where

$$n = b \sqrt{\frac{\omega_m \rho_o C v_o}{2k}}, \quad (20)$$

with k = conductivity of gas,

$\omega_m = 2\pi f_m$, f_m = frequency in cycles per sec. at maximum amplitude,

$\rho_o = \frac{1}{v_o}$ = density,

b = radius of a sphere equivalent to one of the gas volumes.

The subscripts "o" refer to the state when the piston is in its position of equilibrium ($x = 0$).

Substituting (19) into (11) and combining with (14) and (3)

$$\Delta \bar{P} = -2v_o \left(\frac{\partial \bar{P}}{\partial v} \right)_T \frac{a}{V_o} \left[\left\{ \gamma - (\gamma - 1) \frac{3}{2n} \right\} x - \frac{3}{2\omega_m n^2} (\gamma - 1) (1 - n) \dot{x} \right] \\ = (\Delta P)_x + (\Delta P)_\dot{x}. \quad (21)$$

Then†

$$\left. \begin{aligned} (\Delta P)_x &= -2v_o \left(\frac{\partial \bar{P}}{\partial v} \right)_T \frac{a}{V_o} \left[\gamma - (\gamma - 1) \frac{3}{2n} \right] x \\ (\Delta P)_\dot{x} &= \frac{3}{\omega_m n^2} v_o \left(\frac{\partial \bar{P}}{\partial v} \right)_T \frac{a}{V_o} (\gamma - 1) (1 - n) \dot{x} \end{aligned} \right\} \quad (22)$$

Solution for γ

Introducing (22) into (7) and solving for γ we get

$$\gamma = -\frac{m + m_g}{2a^2} \frac{V_o}{v_o} \left(\frac{\partial \bar{v}}{\partial \bar{P}} \right)_T \left(\omega_m^2 + \frac{\beta'^2}{2} \right) + (\gamma - 1) \frac{3}{2n}. \quad (23)$$

* This equation is also readily obtained from Reech's theorem

$$\left(\frac{\partial P}{\partial v} \right)_Q = \gamma \left(\frac{\partial P}{\partial v} \right)_T$$

which may be written as $dP = \gamma \left(\frac{\partial P}{\partial v} \right)_T dv$ for an adiabatic transformation.

† It is interesting to note that if $k = 0$, (21) reduces to the adiabatic equation (18).

Now let

$$\Lambda = \frac{m + m_o}{m} \quad \text{effective mass of the oscillating system as compared to the mass of the piston only.} \quad (24)$$

$$\chi = \frac{\omega_m^2 + \frac{\beta'^2}{2}}{\omega_m^2} \quad \text{displacement of } \omega_n \text{ from the point of maximum amplitude caused by the friction term } \beta'. \quad (25)$$

$$G = -\frac{P_o}{v_o} \left(\frac{\partial \bar{v}}{\partial P} \right)_T \quad \text{departure of the gas from the law } Pv = RT. \quad (26)$$

$$\Delta\gamma = (\gamma - 1) \frac{3}{2n} = (\gamma - 1) \frac{3}{b} \sqrt{\frac{k}{2\rho_o C_v \omega_m}} \quad \text{correction for non-adiabatic compressions.*} \quad (27)$$

Then

$$\gamma_{\text{corr.}} = \frac{m V_o}{2a^2 P_o} \omega_m^2 \Lambda \chi G + \Delta\gamma = \gamma_{\text{exp.}} \chi G + \Delta\gamma, \quad (28)$$

where

$$\gamma_{\text{exp.}} = \frac{m V_o}{2a^2 P_o} \omega_m^2 \Lambda. \quad (29)$$

It is seen that $\gamma_{\text{exp.}}$ is the value of γ that would be obtained if the gas obeyed the equation $Pv = RT$, the piston were not subject to friction β' , and the compressions were strictly adiabatic.

Solution for ω_m and χ

ω_m may be found by locating the frequency for which the amplitude is a maximum, or it may be evaluated in the following more accurate graphical manner. (χ may also be evaluated graphically.)

Let ω_1 = any particular frequency with corresponding amplitude x_1 ,

ω_2 = any particular frequency with corresponding amplitude x_2 ,

ω_m = frequency at maximum amplitude x_m ,

ω_n = natural frequency of system with amplitude x_n .

If ω_1 and ω_2 are chosen, on opposite sides of ω_m , so that $x_1 = x_2$, then by Equation (6)

$$\frac{\omega_1^2 + \omega_2^2}{2} = \omega_n^2 - \frac{\beta'^2}{2}. \quad (30)$$

* It is interesting to notice that according to Kirchhoff (12) the correction term $(\gamma - 1) \frac{3}{b} \sqrt{\frac{k}{2\rho_o C_v \omega_m}}$ also appears in the velocity-of-sound method of measuring γ , this time as a correction in the velocity of sound due to the effects of the tube walls

$$V = V' + \frac{V'}{2} \left[\frac{1}{b} \sqrt{\frac{\eta}{\rho \pi f}} + \left(\frac{\gamma - 1}{\sqrt{\gamma}} \right) \frac{2}{b} \sqrt{\frac{k}{2\rho C_v \omega}} \right],$$

where V = true velocity in free gas,

V' = observed velocity in tube,

b = radius of tube,

η = coefficient of viscosity,

and the other terms have the usual meaning.

For a tube, the ratio $\frac{\text{radiating area}}{\text{volume}}$ is given by $\frac{2\pi bl}{2\pi b^2 l} = \frac{2}{b}$, instead of $3/b$ for a sphere. The term involving the coefficient of viscosity does not enter into the equation used here because the dimensions of the gas container are small compared with the velocity of sound.

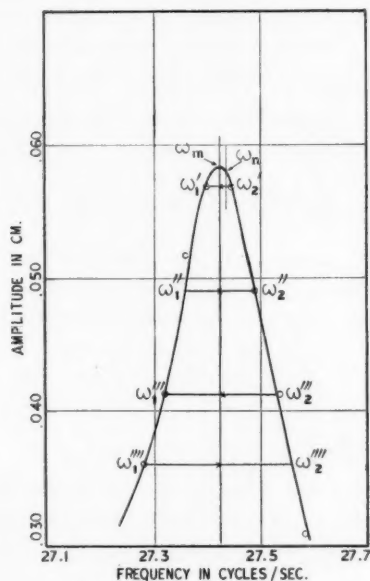


FIG. 3. Resonance curve.

Combining with (7) gives*

$$\omega_m^2 = \frac{\omega_1^2 + \omega_2^2}{2}. \quad (31)$$

Thus if we measure ω_1 and ω_2 at the same amplitude on either side of resonance, ω_m is readily obtained.

Fig. 3 illustrates this method of determining ω_m . The graph was drawn from measurements on air at atmospheric pressure. Table I shows how various values of ω_m thus determined are distributed about the mean value.

TABLE I
FREQUENCY AT MAXIMUM AMPLITUDE
($\omega_m = 2\pi f_m$)

Amplitude	f_1	f_2	f_m
0.0361	27.281	27.560	27.421
0.0413	27.322	27.536	27.429
0.0491	27.359	27.491	27.425
0.0569	27.404	27.450	27.427

Mean value

27.425

Maximum departure from the mean value = 0.016%.

* This equation is also true for the case of dry friction, $\beta' \dot{x} = \pm F$, where F is a constant.

From Equation (6)

$$x_1 = \frac{K'}{\sqrt{(\omega_n^2 - \omega_1^2)^2 + \beta'^2 \omega_1^2}} \quad (32)$$

and

$$x_n = \frac{K'}{\beta' \omega_n} \quad (33)$$

Combining (32) and (33) and placing

$$\omega_n^2 - \omega_1^2 = (\omega_n + \omega_1)(\omega_n - \omega_1) = 2\omega_n(\omega_n - \omega_1) \quad (34)$$

we get

$$\frac{\beta'^2}{2} = 2 \frac{(\omega_n - \omega_1)^2}{\left(\frac{x_n}{x_1}\right)^2 - \left(\frac{\omega_1}{\omega_n}\right)^2}, \quad (35)$$

giving

$$\begin{aligned} \chi &= 1 + \frac{1}{\omega_m^2} \frac{\beta'^2}{2} = 1 + 2 \left(\frac{\omega_n - \omega_1}{\omega_m} \right)^2 \frac{1}{\left(\frac{x_n}{x_1}\right)^2 - \left(\frac{\omega_1}{\omega_n}\right)^2} \\ &= 1 + 2 \left(\frac{f_n - f_1}{f_m} \right)^2 \frac{1}{\left(\frac{x_n}{x_1}\right)^2 - \left(\frac{f_1}{f_n}\right)^2}. \end{aligned} \quad (36)$$

Here ω_n is unknown, but according to Equation (7), since β' is small we may replace it by ω_m as a first approximation where ω_m is determined by (31), then using the value of $\beta'^2/2$ obtained from (35) we may determine ω_n by means of Equation (7). Now using this value in (35) again, $\beta'^2/2$ is obtained to a second approximation. The process may be repeated to any degree of accuracy. χ is finally obtained from (36).

Correction for Loss of Heat by Conduction, $\Delta\gamma$

$\Delta\gamma$ is a correction necessary owing to the fact that the compressions are not strictly adiabatic. The deduction of this correction is based on the assumption that the gas volumes are spherical in shape while the volumes in the apparatus used are cylindrical in shape. Since the radiating area per unit volume is less for a sphere than for a cylinder, one would expect that the correction as given would be too small. This was actually found to be the case. Thus for hydrogen and helium, the conductivity of which is great, this calculated correction is undoubtedly too small in value at the lower frequencies. At higher frequencies (over 50 cycles per sec.) for all gases, and at all frequencies used for less highly conducting gases, the correction is sufficiently accurate as it is very small in absolute value.

It may be shown that the factor $3/b$ in the correction arises from the ratio $\frac{\text{radiating area}}{\text{gas volume}}$ (for a sphere $\frac{4\pi b^2}{4/3\pi b^3} = \frac{3}{b}$). So that in the work described here it would be more accurate to replace this factor by the true ratio, $\frac{F_o}{V_o}$, so that

$$\Delta\gamma = (\gamma - 1) \frac{F_o}{V_o} \sqrt{\frac{k}{2\rho_o C_v \omega_m}} \quad (37)$$

For the apparatus used, this ratio, $\frac{F_o}{V_o}$, is 1.241.

Apparatus Design and Construction

The experimental set-up for this method of measuring γ requires, along with the resonator itself, a supply of low frequency alternating current, a frequency measuring device, an accurate pressure gauge and a means of handling the compressed gases. The variable frequency oscillator, capable of generating currents at frequencies of 15 to 200 cycles per sec., and the frequency measuring device have been described in a previous paper (2). These were used throughout the research with only slight modifications.

Resonator

The essential features of the resonator construction are shown in Fig. 4. Although the work extended only to 25 atm. pressure, the resonator has been

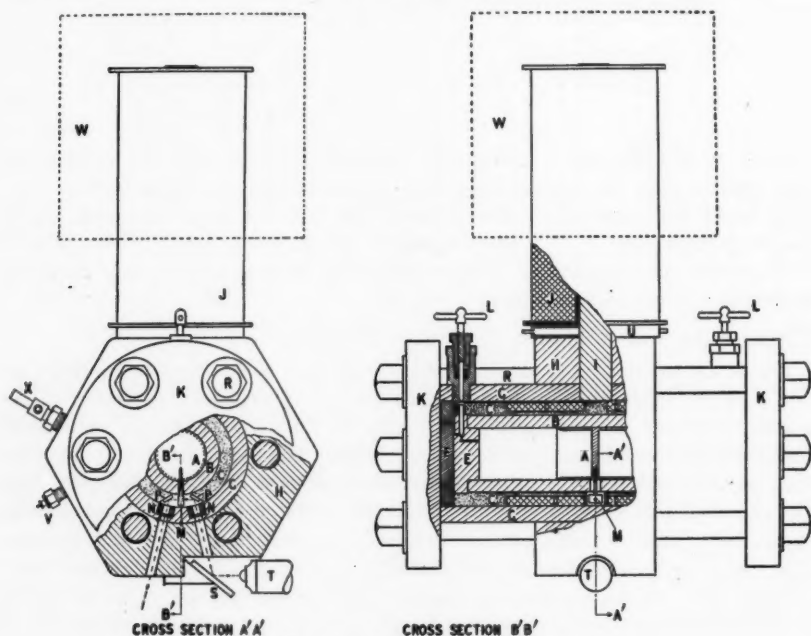


FIG. 4. Complete resonator.

tested up to 1,200 lb. per sq. in. and would probably withstand more. The resonator proper is enclosed in the pressure chamber formed by the brass tube *G* and the end plates *K*. This chamber carries the full strain of the high pressure. *G* is reinforced with a cast bronze hexagonal ring *H* and the end plates *K* are clamped into place with six $\frac{3}{4}$ -in. phosphor-bronze rods *R*. The round tongue and groove joint between *K* and *G* in which a thin rubber ring had been placed forms the gas tight seal.

The resonator proper consists of the cylinder *B*, closed at the ends by the plates *E*, the piston *A*, and the actuating coils *DD* wound on tube *C*. This

tube carries two small mirrors PP whose function will be described presently. The walls of the resonator are not subject to any distorting force, as the pressure inside is balanced by that outside. The plates FF hold the resonator securely in place and keep it from vibrating as a whole.

The piston A was made of carefully annealed steel (annealed to avoid changes in dimensions due to ageing), covered with about 0.007 cm. chromium plate, then ground and lapped. The chromium surface possesses the desirable properties of extreme hardness and low coefficient of friction. The cylinder B was machined from a piece of pressure-cast bronze and also carefully lapped to size until it was of mirror-like finish.

The diameter of the cylinder bore, as measured with a carefully made plug gauge and checked directly with a set of standard Johansson gauge blocks, was found to be 4.0000 ± 0.0001 cm.; the piston diameter was slightly less, 3.9992 ± 0.0001 cm. leaving 4/10,000 cm. all-round clearance. In spite of this close fit, the piston when suspended by the lift magnet moved freely, requiring less than a fraction of a watt power to keep it oscillating. No lubricating oil was used.*

The brass tube C was machined out in two places to carry the actuating coils DD ; the alternating current flowing through these coils causes the piston to oscillate. These coils were each wound with 15,000 turns of No. 34 enamel-covered wire, impregnated in vacuum with Harvel transformer varnish and baked for eight hours at 110°C .

The gas under investigation, subjected to the compressions of the piston A , is enclosed in the two spaces formed by the inner tube (cylinder) B , the ends E , and the piston itself. These spaces are shut off from the rest of the apparatus by the valves L , as shown. Each valve is made in two parts to facilitate dismantling the apparatus.

As pointed out before, the lift-magnet J counterbalances the weight of A , thereby reducing friction. The core I of this magnet is made of Swedish charcoal iron and is screwed into place through the casting H and the tube G . The magnet coil is wound with 8,500 turns of No. 22 S.C.C. wire. The small water-jacket U placed between the lift magnet coil and the casting H serves to carry off the heat generated in this coil.

The amplitude of the motion of the piston is measured with the micrometer eyepiece microscope T through the optical system shown in the end-view. The light comes up through a hole in H , passes through a small round glass window N in G , is reflected by mirror P through a hole in the indicator M (attached to the piston A), reflected by the second mirror P through another window N , and is finally reflected by a mirror S into the microscope. The motion of the indicator M is seen in the microscope as a narrow band of light, formed by the hole, through which the light passes.

* It was found that even the finest lubricating oil formed a film sufficiently thick to wedge the piston tightly in the cylinder.

The vacuum pump and the gas supply are joined to the apparatus by the connection *X*, and the electrical current to the actuating coils *DD* passes through the binding post *V*.

The whole apparatus is connected through a suitable arrangement of valves to a vacuum pump, gas supply, and a manually operated mercury compression pump. By this arrangement it is possible to evacuate the resonator, introduce the gas under any desired pressure up to 50 atm. and return this gas to the storing cylinder after the completion of the test. Actually it was not found necessary to use the compression pump in this work, as all the gases investigated were obtained in a purified form under pressure, and after the completion of a test the gas was allowed to escape into the air. The mercury-operated compression pump will, however, be necessary in the handling of rare and costly gases.

Pressure Gauge

Since the pressure enters as an explicit function into the equation of γ , it is necessary to measure it very accurately if reliable values are to be obtained. For this reason great care was taken in setting up the pressure gauge.

An old Amagat free-piston manometer was completely overhauled, fitted with new pistons and an electrical contact to determine the height of the mercury level within the gauge at any pressure. The cylinders of the old gauge were reground and relapped to remove any distortion caused by the ageing of the steel. New pistons were made of carefully annealed pieces of steel, chromium plated, ground, and lapped to a mirrorlike finish. The diameters of the cylinder bores, as measured with specially made plug gauges, and the diameters of the pistons are as follows:

	<i>Cylinder</i>	<i>Piston</i>
Small	1.02686 cm.	1.02654 cm.
Large	5.00431 cm.	5.00329 cm.

All measurements were made at room temperature with a micrometer reading to 1/10,000 in. and checked against a standard set of gauge blocks. According to the work of P. W. Bridgeman the effective diameter of a piston is the piston diameter increased by one-half the clearance; thus we obtain:

Effective diameter of small piston	1.02670 cm.
Effective diameter of large piston	5.00380 cm.

The ratio of the pressures acting on the two pistons is proportional to the ratios of their areas or the diameters squared, giving this factor as 23.7527. It was possible to locate the mercury surface with the electrical contact, when connected to a triode and earphones, consistently to within 0.001 cm. Measurements were taken only during the "make" of the contact. The height of the mercury column was measured with a cathetometer and a steel scale placed close to the gauge. The scale could be read directly to 0.1 cm. and interpolated with the cathetometer to 0.001 cm. The readings, however, were consistent to only plus or minus 0.010 cm. ($0.010 \times 23.7527 = 0.24$ cm. of mercury pressure). Below 5 atm. the pressure was measured with an open mercury manometer.

Barometer

To obtain reliable values of γ at atmospheric pressure, it is necessary to have an accurate barometer. It was found that the Fortin type barometers at hand were not sufficiently accurate and a home-made barometer was built according to the instructions given by Travers, Senter, and Jaquerod (19). This was placed near the steel scale used with the Amagat gauge so that it could be read directly with the cathetometer.

During atmospheric pressure measurements, the resonator was open to the air through an open-tube oil manometer. By this means it was possible to check the pressure in the resonator without allowing air to contaminate the gas under investigation.

Note on the Design of a Resonator

In designing a resonator two things should be taken into consideration:

- (a) The dimensions of its component parts should be so proportioned that it will operate in a desired range of frequencies for a given range of pressures,
- (b) These proportions should also be those most favourable for sharp resonance.

According to Equation (28), if the small correction factors are neglected

$$\gamma = \frac{2\pi^2 m V_o f_m^2}{a^2 P_o} \quad (38)$$

Thus, for a given f_m^2/P_o ratio and γ it is possible to determine the most suitable values of m , V_o and a . The choice of these values will also be governed by the equation for sharp resonance.

Equation (6) may be written.

$$x = \frac{K'/\omega_n^2}{\sqrt{\left(1 - \left(\frac{\omega}{\omega_n}\right)^2\right)^2 + \left(\frac{\beta'}{\omega_n}\right)^2 \left(\frac{\omega}{\omega_n}\right)^2}} \sin \omega t. \quad (39)$$

The factor β'/ω_n determines the sharpness of resonance, since at $\omega = \omega_n$, the magnitude of x is governed by this factor. The smaller the factor, the greater is the amplitude of oscillations. Then, for sharp resonance, β'/ω_n should be small.

From Equations (5) we may write

$$\left. \begin{aligned} \beta' &\cong \beta/m \\ n &\cong \frac{a(\Delta P)x}{xm} \end{aligned} \right\} \quad (40)$$

Also, by Equation (18), for pure adiabatic changes

$$(\Delta P)_z = -2\gamma v_o \left(\frac{\partial P}{\partial v} \right)_T \frac{ax}{V_o}, \quad (41)$$

which for the ideal gas may be written

$$(\Delta P)_z = 2\gamma P_o \frac{ax}{V_o}. \quad (42)$$

Combining (40) and (42)

$$\frac{\beta'}{\omega_n} \cong \beta \sqrt{\frac{V_o}{2\gamma P_o a^2 m}} \quad (43)$$

Thus for sharp resonance:

β should be small (lift magnet and chromium plated piston),

V_o should be small,

m and a should be large.

Values of m , V , and a were chosen to satisfy both Equation (38) and the above conditions.

It is interesting to notice that according to Equation (43) for a given apparatus, resonance becomes sharper as the pressure increases. This was found to be the case.

Experimental Procedure and Calculation of γ

Filling Resonator

Before filling the apparatus with the gas to be investigated it was evacuated continuously for a number of hours to less than 0.01 cm. of mercury, after which it was flushed with the gas at least three times, being evacuated between each flushing and finally filled to the highest pressure. Readings were taken from the highest pressure down, and the excess gas between each set of readings was allowed to escape to the atmosphere through a needle valve.

Frequency at Maximum Amplitude, ω_m

At the higher pressures (above 5 atm.) it was found that resonance was so sharp that it was possible to obtain the frequency of maximum amplitude by simply recording two frequencies of equal amplitude on either side of resonance and taking the root mean square value [see Equation (31)]. The fact that resonance should become more critical at the higher pressures was pointed out in the discussion of Equation (43).

For pressures lower than 5 atm., a resonance curve similar to that shown in Fig. 3 was plotted for each pressure investigated, and ω_m was obtained by taking the average of a number of root mean square values taken at different amplitudes on the curve.

Apparatus Constants

The constants of the apparatus involved in the calculation of γ , as given by Equation (28), were found to be:

Weight of piston, $m = 143.690 \pm 0.002$ gm.

Area of piston (effective), $a = 12.5639 \pm 0.0005$ sq. cm.

Volume of gas, $V_o = 104.02 \pm 0.02$ cc.

A set of weights, standardized by the U.S. Bureau of Standards, was used in weighing the piston. The effective area of the piston was calculated from the mean of the piston and cylinder diameters (3.9996 cm.; see section on description of resonator). Careful measurements of the length of cylinder B (Fig. 4) and the ends E , combined with the cylinder diameter, gave the total volume of the cylinder.* V_o was obtained by subtracting the volume of

* All measurements of length were made at room temperature. The effects of temperature changes on these dimensions cancel each other in the final equation for γ , since at any temperature t

$$\gamma \propto \frac{V_o}{a t^2} = \frac{V_o (1 + \alpha_1 \Delta t)}{a t^2 (1 + \alpha_2 \Delta t)^2},$$

where t' is the room temperature.

For bronze, $\alpha_1 = 0.553 \times 10^{-4}$ (volume coefficient of expansion).

For steel, $\alpha_2 = 0.240 \times 10^{-4}$ (area coefficient of expansion).

Thus

$$\frac{(1 + \alpha_1 \Delta t)}{(1 + \alpha_2 \Delta t)^2} = \frac{1 + 0.000055 \Delta t}{1 + 0.000048 \Delta t} = 1,$$

if Δt is small.

the piston, found by weighing in water, from the total volume and dividing by 2.

Introducing these constants into Equation (28) gives

$$\gamma_{\text{corr.}} = 1.86907 \times 10^3 \frac{f_m^2}{P_0} \Lambda \chi G + \Delta \gamma, \quad (44)$$

where f_m is measured in cycles per second, P_0 in dynes per square centimetre, and Λ , χ , G , and $\Delta \gamma$ are dimensionless quantities.

For Kingston (lat. $44^\circ 14.6'$) the acceleration due to gravity is 980.530 cm. per sec.², and 1 cm. of mercury at $0^\circ \text{C.} = 13.59509 \times 980.530 = 1.333040 \times 10^4$ dynes per cm.²

Thus

$$\gamma_{\text{corr.}} = 0.14021 \frac{f_m^2}{h} \Lambda \chi G + \Delta \gamma \quad (45)$$

with h measured in centimetres of mercury at 0°C. This is the equation used throughout the research.

Calculation of γ

After measuring the resonance frequencies corresponding to various pressures for a certain gas, it is necessary to evaluate the correction factors Λ , χ , G , and $\Delta \gamma$ to obtain the final corrected values of $\gamma_{\text{corr.}}$

χ is evaluated graphically from the resonance curves by means of Equation (36) and the method of approximations already described.

G is evaluated from Pv data or an empirical equation of state. If the Pv data are represented by an equation of the Holborn and Otto form

$$Pv = RT + BP + CP^2 + DP^3 \quad (46)$$

then by Equation (26)

$$G = -\frac{P}{v} \left(\frac{\partial v}{\partial P} \right)_T = \frac{RT - CP^2 - 2DP^3}{Pv} \quad (47)$$

On the other hand if the Kamerlingh Onnes equation is used

$$Pv = RT + \frac{B}{v} + \frac{C}{v^2} + \frac{D}{v^4} \quad (48)$$

Then

$$G = \frac{Pv}{2Pv - RT + \frac{C}{v^2} + 3\frac{D}{v^4}} \quad (49)$$

To calculate Λ , the value of m_θ at any particular pressure is obtained from the corresponding value of Pv by the equation $m_\theta = 104.02 \frac{P}{(Pv)} \text{ gm.}$

Since v is usually expressed in Amagat units it is necessary to change to cubic centimetres per gram by multiplying by an appropriate factor. This factor may be readily calculated from the value of RT on the zero isothermal as outlined in a recent paper by Deming and Deming (3).

$\Delta\gamma$ is calculated by means of Equation (27). Its value used in this equation is obtained by the method of approximations; using the theoretical value of γ (monatomic 1.666, diatomic 1.400, etc.), $\Delta\gamma$ is calculated approximately. This, when substituted into (45) gives γ to a second approximation. The process may be repeated to any degree of accuracy. In practice it was found that if the γ -pressure curve is plotted as the values are calculated, it is possible after the first few points to extrapolate the value of γ at the next pressure with sufficient accuracy, and $\Delta\gamma$ can be calculated directly.

(Part II will appear in the March issue.)

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THE EQUILIBRIUM PRESSURES OF OXYGEN ADSORBED ON ACTIVATED CHARCOAL¹

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Abstract

Oxygen chemisorbed on activated cocoanut charcoal at 20° C. was found to exert no measurable equilibrium pressure. The small residual pressures obtained under experimental conditions were shown to be due to the presence of slight impurities in the oxygen employed. The impurities responsible for these residual pressures were largely nitrogen and accompanying rare gases.

The velocity of chemisorption of oxygen decreased rapidly with increase in its concentration on the charcoal, approaching a limiting zero velocity at a concentration of 84×10^{-6} moles per gm. This coincides with the concentration at which the heat of adsorption drops rapidly to the limiting value obtained for physical adsorption.

After this limiting concentration was reached, adsorbed oxygen showed true equilibrium with the gas phase. For small additional increases in concentration, the equilibrium pressure was found to increase as a linear function of the concentration, with a proportionality constant of 0.276 mm. per micromole. This represents physical adsorption as compared to chemisorption for lower oxygen concentrations.

Introduction

When oxygen is admitted at room temperature to activated charcoal, and the latter is outgassed as thoroughly as possible, the pressure drops rapidly to a very low value. The relation between this pressure and the concentration of the adsorbed gas was found in this laboratory to be linear for low gas concentrations. For instance, Guy Waddington (10) found the slope of this curve to be 2×10^{-5} mm. per micromole per gm. Later, Lyle A. Swain (8) found a slope of 3×10^{-6} mm. per micromole per gm.

The results of this last investigation made it appear possible that the gas producing this pressure was not oxygen, but an impurity present in the oxygen originally added. Additional support for the conclusion that the residual pressure is not due to oxygen is afforded by a consideration of its high heat of adsorption on charcoal. Such a surface complex should have a dissociation pressure at room temperature not measurable by experimental means.

In the present investigation an attempt has been made to determine the nature of this residual gas pressure and so decide the question raised above. For this purpose, an apparatus was devised whereby the gas could be pumped off the charcoal down to immeasurably low pressures, its quantity estimated, and its composition determined.

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Apparatus

The apparatus consisted of three principal parts: (1) a means of measuring the residual pressure, after introducing a known quantity of oxygen into the charcoal, (2) a device to remove the residual gas from the charcoal down to the lowest pressure attainable with a diffusion pump, and to collect it for measurement and analysis, (3) a micro gas analysis apparatus to determine the composition of the minute quantities of residual gas obtained.

Part (1) of the apparatus is shown in Fig. 1. The charcoal was contained in the quartz bulb, *C*, attached to the remainder of the apparatus by a quartz-to-Pyrex graded seal at *B*. Stopcocks were used only where mercury cutoffs were not practicable. Although these stopcocks were lubricated with Apiezon low pressure stopcock grease, contact of the charcoal for long periods of time with any possible vapour from the grease was prevented by the cutoffs at *A* and *D*.

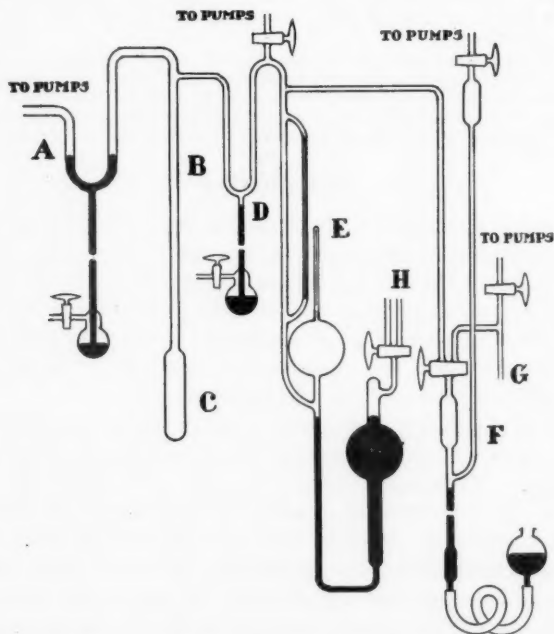


FIG. 1. Apparatus for measurement of concentration and pressure.

The pressures were measured by means of a large McLeod gauge, *E*. The large bulb of this gauge had a capacity of 550 cc. The mercury was raised and lowered by vacuum at *H*. The gauge was marked with compression ratios at 10^4 and 10^5 , although by careful manipulation a less accurate reading, with a magnification of 10^6 , could be obtained.

The gas was generated from potassium chlorate containing a small quantity of manganese dioxide. The oxygen generator and storage bulb, not shown in the sketch, were joined to the apparatus at *G*. The generator was first evacuated, a little oxygen generated, and then evacuated once more. By repeating this several times the purest possible oxygen was obtained. The gas was measured in the constant volume gas pipette at *F*. This pipette had a volume of 7.121 cc.

The activated cocoanut charcoal was obtained from the National Carbon Co., and was identical with the charcoal used in previous investigations (5, 6). It was washed with hydrochloric and hydrofluoric acids, and was finally outgassed at 1000° C., using a diffusion pump, in a manner similar to that previously reported (2, 5, 6).

Part (2) of the apparatus, not shown in the sketch, consisted of the diffusion pump used to outgas the charcoal, backed by a Toepler pump in place of the conventional rotary pump. In order to evacuate this combination previous to use, a second diffusion pump, backed by a rotary pump, was employed. By means of this device it was possible to remove the gas so completely from the space above the charcoal that the McLeod gauge indicated apparently zero pressure. At the same time the gas could be collected at a higher pressure to estimate its quantity and composition.

Part (3), the micro gas analysis apparatus, was attached to the high pressure end of the Toepler pump. It consisted essentially of a large McLeod gauge terminating in a number of small chambers of capillary dimensions, containing the necessary reagents for absorbing specific gases. The drop in pressure on the gauge on absorption of a specific gas was a measure of the quantity present. Carbon dioxide was estimated by means of liquid air, carbon monoxide by oxidation over hot copper oxide to carbon dioxide and simultaneous condensation in liquid air. Oxygen was estimated by oxidation of a hot copper filament. Nitrogen was determined as a residual gas, although a small reaction chamber containing metallic calcium made it possible to distinguish between nitrogen and the rare gases. While no hydrogen was present in this investigation, the apparatus has given accurate determinations of this gas as well, using a small palladium tube about 1 mm. in diameter. The complete gas analysis apparatus will be described in a separate publication.

Experimental

Test for Evolution of Gas from Walls and Pump

Before adding oxygen to the charcoal, the Toepler diffusion pump combination, cut off from the charcoal, was operated for considerable periods of time, to determine whether appreciable quantities of gas could be removed continuously from the walls of the apparatus, particularly from the hot parts of the diffusion pump. To determine the volume of this gas, the McLeod gauge incorporated in the micro gas analysis apparatus was calibrated in terms of the volume of gas pumped off. One millimetre on the capillary was found to represent 9.5×10^{-5} cc. of gas.

In 13 hours' pumping a total of 6.52×10^{-4} cc. of gas was collected, only 1.1×10^{-4} cc. of this being collected in the last six hours. Furthermore, it was found that even smaller quantities of gas came off after the apparatus had been in use for a time. Similar observations were made with the cold outgassed charcoal in contact with the pump. Virtually the same amount of gas was collected; this indicated that no residual oxides of carbon evolved at higher temperatures remained on the charcoal.

Measurement of Pressure and Quantity of Residual Gas

A measured quantity of oxygen was then introduced and the pressure measured at various intervals by means of the McLeod gauge until it had dropped to a constant value, the temperature being maintained as close to 20° as possible. The time required for initial additions of oxygen to reach a constant pressure was too short for measurement, but at 58.6 micromoles per gm. it amounted to seven hours.

The residual gas was then pumped off at room temperature with the Toepler diffusion pump combination, until no more gas could be removed. The time necessary to do this varied from 25 to 180 min. The volume of gas obtained was determined by compressing it into the calibrated capillary of the McLeod gauge incorporated in the gas analysis apparatus. Succeeding increments were treated in a similar manner. Above 58.6 micromoles per gm., only rate of adsorption measurements were made. These were continued to 83.5 micromoles per gm., where chemisorption practically ceased.

Results

As such small quantities of gas are involved, the results are reported in terms of micromoles, where one micromole equals 10^{-6} moles. The results are shown in Table I. Column 1 gives c , the concentration on the charcoal in micromoles per gram. Column 2 gives the minimum pressure in millimetres of mercury $\times 10^5$, obtained after the addition of each increment of gas, any free gas from the previous increments having been pumped off. Column 3 gives the total micromoles of oxygen added per increment. Column 4 gives the maximum amount of gas in micromoles $\times 10^3$ that could be pumped off the charcoal after the addition of each increment of oxygen. Column 5 gives the ratio of the amount of gas that could be pumped off to the amount of oxygen added for each increment $\times 10^3$.

It is evident for several reasons that the pressures in Column 2 are not due to oxygen in equilibrium with the gas already adsorbed. First of all, we would expect the pressures to rise with increase in concentration, c , whereas they show no such trend. In addition, the pressures can be reduced virtually to zero by pumping off a minute fraction of the total gas adsorbed, and there is no tendency for this pressure to be re-established on standing. Finally, the fractions pumped off, as shown by Column 5, are more constant than would be expected if the gas were in equilibrium with the main mass of oxygen on the charcoal. It is evident that the gas producing these low pressures is in

TABLE I

RATIOS OF GAS PUMPED OFF TO GAS ORIGINALLY ADDED PER INCREMENT

1	2	3	4	5
$c = O_2$ conc., micromoles per gram	Res. pressure, mm. $\times 10^3$	O_2 per increment, micromoles	Gas pumped off per increment, micromoles $\times 10^3$	(4)/(3) $\times 10^3$
0.7	0.5	21.5	9.33	43.4
2.44	0.7	53.4	2.54	4.75
4.94	0.8	76.8	2.97	3.87
7.30	12.0	72.5	5.94	8.20
8.73	2.3	43.9	8.48	19.31
10.50	1.1	54.4	5.51	10.14
13.7	2.0	98.3	25.45	25.9
17.5	1.6	36.9	9.33	25.3
19.0	2.8	46.1	11.87	25.8
52.1	2.0	193.5	11.87	6.1
58.6	4.8	199.6	48.77	24.4

equilibrium with a small quantity of some foreign gas adsorbed with difficulty by the charcoal, and consequently, removed rather easily at room temperature.

The quantity of gas pumped off after each increment was of the order of 2×10^{-4} cc., which is too small for even micro analysis. However, accumulation of all the gas pumped off, while still rather small in amount, made it possible to demonstrate the absence of oxygen and the oxides of carbon. It apparently consisted entirely of nitrogen and the accompanying rare gases. It is evident that this gas is the result of the accumulation of impurities from the oxygen originally chemisorbed. The absence of the oxides of carbon, which might be expected to be present under these circumstances, can be explained by recent work done in this laboratory which shows that small surface concentrations of the oxides of carbon are very tenaciously held at room temperature by the charcoal. Absolutely pure oxygen, then, when chemisorbed on active charcoal properly outgassed, should give no measurable pressure.

Variation of Rate of Chemisorption with Concentration

It follows from the above conclusion that free oxygen in the gas phase is in equilibrium with physically adsorbed oxygen only. Consequently, the rate of decrease of its equilibrium pressure is a measure of the rate of conversion of physically adsorbed to chemisorbed oxygen. As was pointed out previously, this rate was found to decrease very rapidly with concentration. To get some idea of the relation between these two variables, numerous rate measurements were made at various concentrations up to complete saturation for chemisorbed oxygen.

The pressure ranges over which these rate measurements were made were all within the capacity of the McLeod gauge, the highest being 3.14×10^{-2}

mm. According to data presented later in this paper, this pressure corresponds to only 8.66×10^{-3} micromoles per gm. present as physically adsorbed oxygen, while the total surface capacity for chemisorption is 84 micromoles per gm. Except at concentrations very close to this saturation value, it is evident that the conversion of the above small increment of physically adsorbed oxygen to the chemisorbed state would alter the concentration of the uncombined active centres to a negligible degree. Consequently, whether the velocity of chemisorption is considered to be determined by an energy of activation or by diffusion, it is reasonable to assume, for such small quantities adsorbed per increment, that the rate of conversion of physically adsorbed to chemisorbed oxygen should be proportional to the concentration of physically adsorbed oxygen on the surface. As the equilibrium pressure is a linear function of this concentration over the ranges considered, we can write, $dp/dt = k(p - p_0)$, where k is the velocity constant, p is the equilibrium pressure at the time t , and p_0 is the final pressure at $t = \infty$, due to traces of foreign gases.

If the above equation is written in the form $d \ln(p - p_0)/dt = k$, it is evident that $\log(p - p_0)$ plotted against t should give a straight line, where $k = 2.303 \times \text{slope}$. The experimental values plotted in this way actually do give reasonably straight lines. The values of k so obtained, the values for the time to half-value $t_{1/2} = 0.6932/k$, and the corresponding values of c are tabulated in Table II.

Velocity measurements at the lower concentrations are not reported. They could be measured accurately only by means of a special manometer. Qualitatively it can be stated that initial additions of oxygen are adsorbed almost instantaneously and that the velocity of chemisorption decreases progressively with concentration to the values presented in Table II.

TABLE II
VARIATION OF THE VELOCITY OF CHEMISORPTION WITH CONCENTRATION AT 20° C.

c , micromoles per gram	k , 1/hr.	$t_{1/2}$ hr.	$c \times 10^6$ micromoles per gram	k , 1/hr.	$t_{1/2}$ hr.
40.0	3.16	0.219	72.3	0.102	6.808
45.8	1.05	0.658	80.3	0.034	20.51
58.6	0.464	1.495	83.5	0.012	58.23
61.1	0.380	1.825			

The c and $t_{1/2}$ values of Table II are plotted in Fig. 2. It is evident from the shape of the curve that $t_{1/2}$ increases very rapidly with c in such a way that it tends to become infinite at $c = 84$ micromoles per gm. This represents the limiting concentration for the chemisorption of oxygen on the charcoal. Below this limiting concentration physically adsorbed oxygen is slowly being transformed into chemisorbed oxygen with a continuous drop on the oxygen

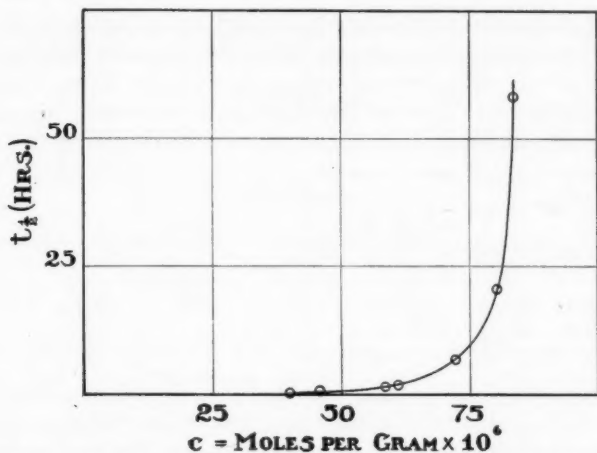


FIG. 2. Variation of the velocity of chemisorption with concentration.

pressure. Above this concentration free oxygen in the gas phase is in true equilibrium with physically adsorbed oxygen on the surface. It is interesting to note that this limiting concentration for chemisorption corresponds very closely to the concentration found by Marshall and Bramston-Cook (5) at which the vertical portion of the heat of adsorption curve intersects the horizontal portion, indicating a sudden change from chemisorption to physical adsorption.

As the affinity of the reaction between oxygen and the carbon surface seems to vary comparatively little over the entire chemisorption range, there is no reason to expect any great variation in a possible energy of activation for this reaction. As the first amounts of oxygen added are adsorbed almost instantaneously, this energy of activation must be very low in this range, and any reasonable increase in its value could hardly account for the very low velocities at the higher concentrations. It would seem, then, that these low velocities are mainly due to increasing inaccessibility of the active carbon centres as the chemisorption proceeds, thus involving some type of diffusion mechanism, activated or otherwise.

Measurement of Equilibrium Pressures of Physically Adsorbed Oxygen

At the higher oxygen concentrations the rate of chemisorption was so slow that it was possible to obtain a measure of the relation between the equilibrium pressure and the concentration of the physically adsorbed oxygen.

At $c = 83.7$ micromoles per gm., where $t_{1/2}$ was 58.23 hr., the equilibrium pressure was 22.1×10^{-3} mm. A small quantity of the gas was pumped off and, on analysis, was found to be oxygen. At the same time, its volume was determined in the gas analysis apparatus. The new pressure was then measured, and the process was repeated several times until the pressure had been reduced to zero. These volumes, converted to the conventional units,

gave the concentration of physically adsorbed oxygen, which we shall call C . In Table III the equilibrium pressures are tabulated with the corresponding values of C .

TABLE III
EQUILIBRIUM PRESSURES FOR PHYSICALLY ADSORBED OXYGEN AT 20° C.

$C = \text{moles} \times 10^6$ per gram	$p, \text{ mm.} \times 10^3$	$C = \text{moles} \times 10^6$ per gram	$p, \text{ mm.} \times 10^3$
0.	0.	0.055	15.3
0.031	8.8	0.080	22.1
0.048	13.1		

In accordance with the limiting form of the Langmuir equation (3) at low pressures, these results show a linear relation when plotted, which can be expressed by the equation $p = a.C$, where $a = 0.276$ mm. per micromole per gm. It is evident that only a very small concentration of oxygen is necessary to give a comparatively high equilibrium pressure in the case of physical adsorption. The contrast with chemisorption is most marked.

For comparison with the above value of a , the initial slope of the isotherm for nitrogen, determined by Titoff (9), was calculated in the present units and gave 0.88 mm. per micromole. Calculation from the measurements of Miss Homfray (1) gave 0.133 mm. per micromole, while the measurements of Rowe (7) gave 0.44 mm. per micromole. The values naturally vary somewhat with the variety and treatment of the charcoal used, but it is interesting to note that the present value for oxygen falls among the values obtained for a characteristic case of physical adsorption involving a gas of approximately the same condensability.

Comparison with Previous Work

The only measurements in the literature, to the writers' knowledge, of the equilibrium pressures of oxygen on activated charcoal at low concentrations are reported by Rowe (7). Unfortunately, Rowe outgassed his charcoal at only 450° C., which is not sufficient to remove any large part of the chemisorbed oxygen from the surface. Also, he did not determine the composition of the gas producing the pressure. His results do not show the virtually complete disappearance of oxygen due to chemisorption, although he noticed the variation of velocity of adsorption with concentration. On the other hand, as would be expected for a partially outgassed charcoal, his values do not agree with those quoted in Table III for physical adsorption. However, at the higher pressures, where physical adsorption undoubtedly existed, the slope of his p - c curve is of the same order as the present value of a .

Lowry and Hulett (4) pumped off excess oxygen from active charcoal with a Toepler pump, and showed that a considerable amount could not be removed in this way, which led them to the conclusion that chemical combination had

taken place. However, as the Toepler pump barely reaches, at its lower limit, the pressures which the writers were investigating, the results could throw no light on the possible existence of equilibrium pressures of this order. On the other hand, the present results could be regarded as a verification, under more exacting conditions, of the conclusion of Lowry and Hulett, if such were needed.

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THE QUENCHING OF MERCURY RESONANCE RADIATION BY ETHYLENE¹

BY E. W. R. STEACIE²

Abstract

An investigation has been made of the quenching of mercury resonance radiation ($\lambda 2537$) by ethylene. A quenching cross-section of $48 \pm 5 \times 10^{-16}$ cm.² was found.

Introduction

A great deal of valuable photochemical information has been obtained by experiments on mercury photosensitization. In the interpretation of such experiments it is essential to know the fate of the absorbed energy, and this can be arrived at only by a determination of the quenching characteristics of the gases involved. In many cases such information was lacking, and it was decided to investigate the quenching of $\lambda 2537$ by a number of gases with which photosensitization experiments have been made. Other circumstances have made it necessary to abandon the work, but sufficient data have been obtained to make a fairly reliable estimate of the quenching cross-section of ethylene. Since no previous data on ethylene are available it was considered desirable to report the results obtained.

Experimental

The experimental arrangement was similar in principle to that employed by Lipson and Mitchell (2). A Hanovia Sc2537 high voltage mercury arc served as the source of mercury resonance radiation. The radiation from the lamp passed through a system of slits and quartz lenses, and was divided into two beams. One of these fell on a Weston photronic cell and a system of filters, so that the intensity of the radiation below 3000\AA could be determined. This intensity was maintained constant by adjusting a rheostat in the primary circuit of the transformer from which the lamp was operated.

The other portion of the light beam passed through a quartz cell with plane windows at right angles to one another meeting at a common edge. The beam passed close to the common edge. The cell contained liquid mercury, and the vapour pressure was maintained at a low constant value by keeping the main portion of the cell in ice in a Dewar flask.

The resonance radiation was taken off at right angles, defined by a slit, and focused on to a photographic plate (Eastman 40). With the cell evacuated calibration marks were first put on the plate using various exposures. The cell was then filled with ethylene to the desired pressure, several hours were

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allowed for the re-establishment of vapour pressure equilibrium, and an exposure was made. The blackenings of the plate were then determined photometrically. (For the present purpose the failure of the reciprocity law is not appreciable.) The quenching, Q , was then taken as the ratio of the intensity of resonance radiation from the cell containing the foreign gas, to that from the evacuated cell.

The resulting values of Q should be an accurate measure of the quenching, since the necessary conditions were fulfilled (3), *viz.*

(a) The use of the lowest possible pressures of the absorbing gas to diminish Lorentz broadening of the absorbing line.

(b) The reduction of "imprisonment" by using a low mercury vapour pressure. (Under the conditions employed the absorption coefficient at the centre of the 2537 line is about 0.7.)

(c) The windows through which the radiation entered and left were near a common edge, so that only a very small portion of the mercury vapour was irradiated.

In view of these conditions the application of the Stern-Volmer equation (4) is justified.

Ethylene of 99.5% purity was obtained in cylinders from the Ohio Chemical and Mfg. Co., and was fractionally distilled in a Podbielniak column before use. Hydrogen was taken from cylinders and passed over hot platinized asbestos and through a liquid air trap.

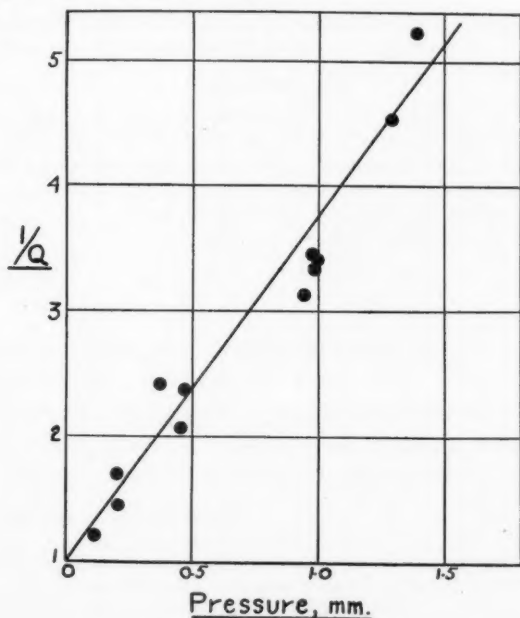


FIG. 1.

Results

The results for ethylene are shown in Fig. 1 in the form of a plot of $1/Q$ against pressure. It will be seen that a good straight line is obtained. From the slope of the line the quenching cross-section is obtained in the usual way from the relation (2),

$$\sigma_q^2 = \frac{1/(Q \cdot p)}{2666.6\tau \left[\frac{2\pi N}{KT} \left(\frac{1}{M_1} + \frac{1}{M_2} \right) \right]^{\frac{1}{2}}},$$

where σ_q^2 is the quenching cross-section, p the pressure in mm., τ the life of the excited state (taken as 1.1×10^{-7} sec. (3)), M_1 and M_2 are the molecular weights of ethylene and mercury, N is Avogadro's number, and K is the gas constant. The value thus obtained is 48×10^{-16} cm.² This is a very high value, but is not out of line with previous values for complex molecules, such as 59.9×10^{-16} cm.² for benzene.

This value furnishes qualitative confirmation for the assumptions of Jungers and Taylor (1) in their work on the mercury photosensitized reactions of ethylene, since it means that hydrogen and ethylene quench mercury resonance radiation with approximately the same efficiency.

As a check on the method, measurements were also made with hydrogen. These gave the result

$$\sigma_q^2 = 8.9 \times 10^{-16} \text{ cm.},$$

in good agreement with Zemansky's (5) value of 8.6×10^{-16} cm.

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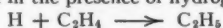
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CADMIUM PHOTOSENSITIZED REACTIONS OF ETHYLENE¹

BY E. W. R. STEACIE² AND ROGER POTVIN³

Abstract

An investigation has been made of the cadmium photosensitized reactions of ethylene and of ethylene-hydrogen mixtures. With ethylene alone the quantum yield of the reaction is very low, viz., about 0.01. With ethylene-hydrogen mixtures the quantum yield is about 0.5 to 0.7 depending upon the conditions. The products of the reaction are methane, ethane, propane, butane, propylene, and higher hydrocarbons. The mechanism of the reaction is discussed and compared with that of the mercury photosensitized reaction. It is concluded that the main steps of the reaction in the presence of hydrogen are



together with radical recombination reactions, and reactions of the type



Introduction

In a previous paper (13) a cadmium resonance lamp of high intensity was described, together with some qualitative preliminary observations on the cadmium photosensitized reaction of hydrogen and ethylene. In a later paper, work on the cadmium photosensitized reactions of ethane was reported (14). The present communication is concerned with further work on the reactions of ethylene, alone and in the presence of hydrogen.

Bates and Taylor (2) first investigated cadmium photosensitized reactions, and reported that in ethylene-hydrogen-cadmium vapour mixtures illuminated with $\lambda 3261$ no hydrogenation to ethane occurred, but that some polymerization of ethylene took place. They showed, however, that hydrogen quenched the resonance radiation, and suggested that it took up the energy of the excited cadmium atom as vibrational energy. Bender (3) investigated the quenching of $\lambda 3261$ by hydrogen, and his results, as well as those on the reactions of ethane, suggest that the mechanism of the quenching is



In other words hydrogen atoms appear to be produced in the process.

Our preliminary results (13) indicated that

"(a) With pure ethylene little or no polymerization occurs.

(b) In ethylene-hydrogen mixtures polymerization of ethylene occurs, and in addition there is considerable hydrogenation."

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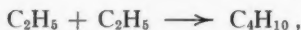
In the case of the ethane decomposition (14) the results indicate that the primary process is a C-H bond split, probably by the reaction



Much work has been done on the mercury photosensitized reactions of ethylene and ethylene-hydrogen mixtures (1, 7, 8, 19). The most comprehensive investigation is that of Jungers and Taylor (6). They concluded that with excess hydrogen the rate is independent of the ethylene pressure. Butane is the most important product, with small amounts of ethane. Negligible amounts of methane are formed. The suggested mechanism involves the reactions



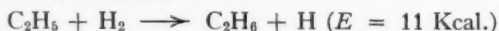
followed by



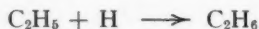
and to a lesser degree the disproportionation reaction



The yield of ethane is low because



and



are not very important at the temperatures used in these experiments. Low methane concentration is evidence of low hydrogen atom concentration since these atoms at ordinary temperatures give considerable C-C bond split with formation of methane. Since not all the resonance radiation is taken by hydrogen, the rate of hydrogenation progressively decreases with decrease of hydrogen content and the character of the reaction changes toward polymerization. When hydrogen is absent there is, in agreement with earlier findings, first a slight pressure increase and then a rapid decrease. The slope of the pressure-time curves is practically the same for ethylene alone and for mixtures of hydrogen and ethylene.

Experimental

The cadmium lamp, reaction vessel, etc., have already been described (14). The reactant gases passed through a cadmium saturator, through the lamp, and then to cooled traps where higher hydrocarbons were removed. The gases were circulated by a magnetically operated pump. The reaction vessel was maintained at 278°C., and the saturator temperature was such as to maintain a cadmium vapour pressure of 0.018 mm. in the system. The output of the lamp on $\lambda 3261$ was approximately 6.4×10^{-6} einsteins per second (see the previous paper for a discussion of the uncertainties involved in the determination of the lamp output).

Analysis

The products of the reaction were pumped by means of a Toepler pump into a portable mercury gas-holder. They were then transferred to a small-capacity low temperature distillation apparatus. In the distillation, hydrogen

and methane were taken off together and analysed by combustion. All fractions were also checked for unsaturated hydrocarbons by conventional methods in a Burrell gas analysis apparatus. In a number of cases only partial analysis could be made owing to the small amount of gas available.

Materials

Cadmium was of c.p. grade and was purified by distillation.

Hydrogen was obtained from commercial cylinders, and was purified by passage over hot platinized asbestos, followed by a liquid-air trap.

Ethylene was obtained in cylinders from the Ohio Chemical and Mfg. Co., and was purified by fractional distillation.

Results

Before the development of the lamp-reaction vessel system referred to above, a few preliminary experiments were made in a simple static system. In these a straight tube cadmium resonance lamp was placed in a furnace close to a small (45 cc.) Corex *D* cylindrical reaction vessel containing cadmium. The source and reaction vessel were surrounded with aluminium foil. Even so, reflection losses were severe, and the light input was comparatively small. In these experiments the quantity of products was too small to analyse, and the reaction was followed merely by pressure change. Before radiating, the entire vessel was cooled down in liquid air and the pressure read. After the run another reading was made under the same conditions.

A blank run was first made. No change in pressure was obtained after heating for 17 hr. at 260° C. a mixture of hydrogen, ethylene, and cadmium vapour. There is therefore no appreciable thermal or catalytic reaction at this temperature. The data of a number of runs in the static system are given in Fig. 1.

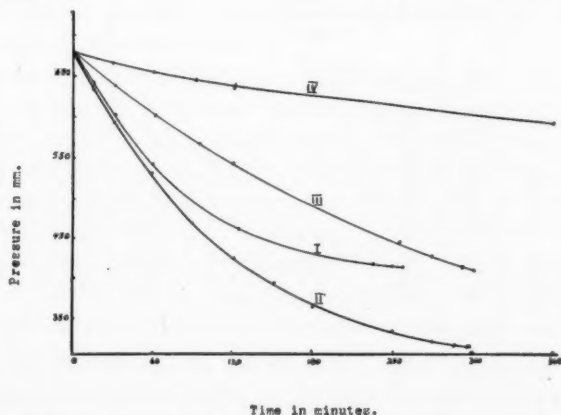


FIG. 1. The pressure change in the cadmium photosensitized reactions of ethylene and hydrogen. Temperature, 260° C.

Curve I. $1\text{H}_2 + 1\text{C}_2\text{H}_4$
Curve II. $1\text{H}_2 + 3\text{C}_2\text{H}_4$

Curve III. $1\text{H}_2 + 7\text{C}_2\text{H}_4$
Curve IV. $1\text{H}_2 + 15\text{C}_2\text{H}_4$

As may be seen from Fig. 1, for mixtures high in ethylene, the rate of pressure change is strongly dependent on the hydrogen concentration. In the case of a 1 : 1 hydrogen-ethylene mixture nearly half the initial amount of hydrogen is consumed in the reaction. Polymerization of ethylene and hydrogenation are therefore competing on approximately equal terms. The very small reaction in the absence of much hydrogen is striking by comparison with the results of investigations of the mercury photosensitized reactions of ethylene. A more detailed examination of the reaction was therefore made in a circulatory system. The results are given in Tables I and II.

TABLE I

CADMIUM PHOTOSENSITIZED REACTIONS OF ETHYLENE AND HYDROGEN

Circulatory system. Temperature, 278° C.

Cadmium vapour pressure, 0.018 mm.

 λ_{3261} absorbed, 6.4×10^{-6} einsteins per sec.

Volume of system, 2400 cc. in Runs 1 to 13, 1700 cc. in Runs 14 to 16.

Circulation rate, 2400 cc./min.

Run No.	Time, min.	Initial pressures, mm.		Pressure decrease, mm.	Experimental conditions	Fraction reacting		Moles of H ₂ consumed per sec. $\times 10^6$	Moles of C ₂ H ₄ consumed per sec. $\times 10^6$	Quantum yield
		H ₂	C ₂ H ₄			of C ₂ H ₄	of H ₂			
1	300	—	201	0	Lamp on, no Cd vapour in reaction system.	0.0	—	—	—	—
2	120	100	100	0		0.0	0.0	—	—	—
3	360	100	100	0	Cd vapour in system. Lamp off.	0.0	0.0	—	—	—
4	420	—	200	0		0.0	—	—	—	—
5	60	—	200	0	Trap at room temperature	Not detectable		—	—	—
6	260	—	253	12		0.03	—	—	0.05	0.01
7	360	—	250	14		0.05	—	—	0.06	~0.01
14	1440	—	294	62		0.37	—	—	0.13	0.02
15	50	14	200	27		0.27	~1.0	0.46	1.8	0.28
16	300	14	200	72	Trap at -131° C.	0.80	1.0	0.08	0.9	0.14
8	8	100	100	18		0.23	0.19	3.6	4.5	0.70
9	16	97	97	36		0.49	0.27	2.4	4.5	0.70
10	100	230	230	223		0.97	0.48	1.7	2.9	0.45
11	30	100	128	168		0.61	0.31	1.5	3.8	0.59
12	75	100	256	166		0.76	0.51	1.1	3.9	0.60
13	90	150	390	230		0.57	0.66	1.5	3.7	0.58

It will be seen from Table I, that in the absence of hydrogen very little reaction occurs. In Runs 15 and 16, in which the quantity of hydrogen is small, there is a comparatively rapid pressure decrease until all the hydrogen is used up and then a slow further decrease. In runs made without hydrogen, however, the pressure decrease is slow but approximately linear. The small

TABLE II
THE PRODUCTS OF THE REACTION

Run No.	Gaseous products in mole per cent								Liquid products as weight per cent of total products*
	H ₂	CH ₄	C ₂ H ₆	C ₃ H ₈	C ₄ H ₁₀	C ₄ H ₈	C ₂ H ₄	Heavy unsaturated hydrocarbons, mainly C ₄ H ₆	
1	-	-	-	-	-	-	-	-	-
2	-	-	-	-	-	-	-	-	-
3	-	-	-	-	-	-	-	-	-
4	-	-	-	-	-	-	-	-	-
5	-	-	-	-	-	-	-	Trace	Trace Present, not determined
6	-	-	-	-	-	-	-	Trace	
7	-	-	-	-	-	-	-	Trace	
14	-	-	-	-	-	-	-	Present	
15	-	Present	Trace	{ Present in considerable amount				{ Present in considerable amount	36.3
16	-	Present	Trace						58.8
8	-	8.0	Trace	-	92.0		-	Trace	Present, not determined
9	-	13.5	6.4	-	23.0	53.3	-	3.8	
10	-	20.0	33.5	-	16.0	27.0	-	3.5	41
11	-	Trace	Trace	1.5	17.0	59.0	-	22.5	-
12	-	3.8	15.0	4.6	14.5	32.1	-	30.0	36
13	-	0.5	19.5	5.5	14.0	31.0	-	20.5	52

* Partly unsaturated hydrocarbons. By a rough vapour pressure analysis, predominantly C₄. Some heavier polymer also present.

reaction "in the absence of hydrogen" is therefore a real effect and is not merely due to traces of hydrogen present as an impurity in the ethylene.

In view of the above facts the quantum yield in hydrogen-ethylene mixtures is significant only in the early stages of the reaction, as in Runs 8 and 9, and thus has a value slightly less than 1.

As shown in Table II, large amounts of liquid products, and of butylene are found. Lighter hydrocarbons, both saturated and unsaturated, are also present. In view of the wide range and of the relatively small amount of gaseous products, the analyses for the lower hydrocarbons are not very satisfactory. However, the results show that the amount of methane in the gaseous products increases with increasing time of exposure, and that it is decreased strongly by trapping out the heavier products. Propane and butane are present in relatively large amounts throughout. As might be expected, butylene survives in much larger amounts when it is protected from further attack by trapping out.

Fig. 2 shows a typical pressure-time curve for a run in the circulatory system. As will be seen, the rate of pressure decrease diminishes as the reaction proceeds, owing to the diminution in the concentrations of ethylene and hydrogen and to the increased importance of secondary reactions.

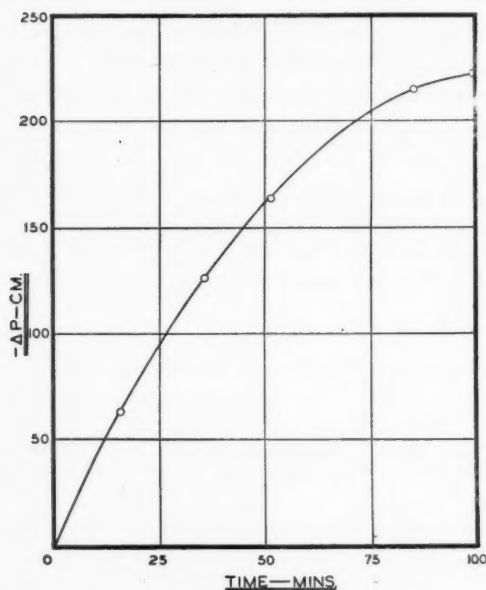


FIG. 2. Pressure-time curve for Run No. 10.

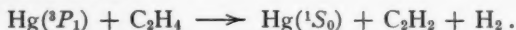
Time, min.	0	16	36	52	86	100
Total pressure, mm.	460	396	333	295	243	237

Discussion

The Reaction in the Absence of Hydrogen

The most notable feature of the above results is the very small quantum yield in the absence of hydrogen. This is in sharp contrast to the results obtained by mercury photosensitization. This is not due to a small amount of hydrogen in the ethylene since the rate is low and constant. If the effect were due to a trace of hydrogen the rate would fall off suddenly when the hydrogen was consumed.

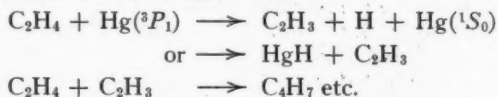
The generally suggested mechanism for the primary step in the *mercury* photosensitized reaction is



This reaction is only slightly endothermic, and hence the low quantum yield in the case of the cadmium photosensitized reaction cannot be ascribed merely to the smaller energy of the quantum. Furthermore, as previously shown (14), quenching of cadmium resonance radiation by ethylene is highly efficient, and the lack of reaction cannot be ascribed to a small quenching efficiency. It is, of course, possible that ethylene molecules might quench 3P_1 cadmium atoms merely to the metastable 3P_0 state, and hence receive far too little energy to cause reaction. However, considering the relatively long life of the 3P_0 state, the small energy difference between the 3P_1 and 3P_0 states,

and the high temperature, it appears likely that if quenching merely occurred to the 3P_0 level, most of the metastable atoms would be raised to the 3P_1 level by collisions of the first kind, and hence the net quenching efficiency would be low. Since this is not the case, it appears probable that ethylene molecules quench the excited cadmium atoms to the ground state, and thus receive a relatively large amount of energy. It is therefore difficult, from this point of view, to explain the large difference between the quantum yields in the mercury and cadmium photosensitized reactions.

However, it is possible that the mercury photosensitized reaction may proceed by a free radical mechanism, such as



If this is so, the analogous reaction in the case of cadmium



would be ruled out on thermochemical grounds if the C-H bond strength in ethylene is somewhat greater than 102 Kcal. There are definite indications that the C-H bond strength in ethylene is higher than that in the paraffins, and while there is great uncertainty as to its actual magnitude, a value somewhat greater than 102 Kcal. is not unlikely.

It is perhaps pertinent to point out that Jungers and Taylor (5) investigated the sodium photosensitized reaction. (The sodium D-line corresponds to 48 Kcal.). They also found efficient quenching by ethylene, but they obtained no polymerization.

The Reaction in the Presence of Hydrogen

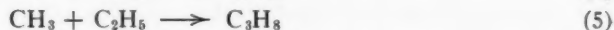
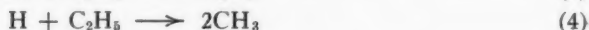
In view of the great difference in the quantum yield of the reaction in the presence and in the absence of hydrogen, there is little doubt that hydrogen must be concerned in the primary process of the reaction of ethylene-hydrogen mixtures. Hence the primary reaction must be



There is ample evidence that hydrogen atoms react rapidly with ethylene (6, 22).



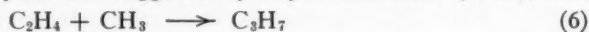
The paraffins produced then presumably arise from reactions such as



etc. etc.

In view of the known efficiency of Reaction (4) (11, 12, 16), it might be expected that much more methane would appear in the products. However, it is well known that ethylene reduces the stationary hydrogen atom concentration to a very low value (16), and hence Reaction (4) does not occur to a very large extent.

There is much evidence that the polymerization of ethylene can be sensitized by free radicals (4, 9, 10, 15, 18, 20, 21). Hence it appears likely that the higher products largely arise as suggested by Taylor and Bates (1, 17), viz.,



etc.

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THE DENSITY OF GASEOUS CHLORINE¹

BY A. S. ROSS² AND O. MAASS³

Abstract

The density of gaseous chlorine has been determined over the temperature range 15° to 75° C. and up to two atmospheres. The values obtained are compared with those extant in the literature, and excellent agreement is found with the very precise measurements of Jaquerod and Tourpaian at 15° C. and 725 mm. pressure. There is also good agreement, over the temperature range of this investigation, with the measurements of Pier at a pressure of one atmosphere. The equation of state proposed by Maass and Mennie is shown to fit the experimental results over the whole range and to give, for temperatures and pressures outside the region covered by this investigation, values of the density of gaseous chlorine that are in good agreement with the results obtained by Jaquerod and Tourpaian, and by Pier. Tables of calculated and experimentally determined densities and apparent molecular weights show the deviations of gaseous chlorine from ideality. The equation of state is given in a convenient form for the calculation of the density of the gas in industrial applications.

Introduction

In an investigation of the solubility of chlorine in water it was found necessary to calculate concentrations involving the absolute densities of gaseous chlorine. Accurate knowledge of the variation of the density over the temperature range between 0° and 100° C. and for pressures from zero to several atmospheres was desirable. The data required were essential in view of the experimental technique to be employed in measuring the solubilities. A survey of the literature disclosed that some very accurate measurements at atmospheric pressure had been made by Jaquerod and Tourpaian (4) over the temperature range 0 to 20° C. and at an average pressure of approximately 725 mm. Inasmuch as these authors used chlorine from three different sources and determined the density of the gas by two methods, volumetric and hydrostatic, their measurements deserve exceptional weight. Other than their data, the only measurements pertinent to the proposed investigation were those of Pier (20), who determined the density at atmospheric pressure over the range 0° to 184° C., at a few scattered temperatures at other pressures, and at 13.5° C. over the pressure range from 0.0569 to 1 atm. In the present investigation, density determinations have been made at 15°, 35°, 50°, and 75° C. and over a pressure range from 20 cm. to 2 atm. The results have been incorporated into an equation of state which is shown to be in agreement with the experimental results. Comparative tables are given of the results of this investigation and of those found by Jaquerod and Tourpaian, and by Pier.

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Experimental

Purification of Chlorine

Chlorine was obtained in a cylinder from Canadian Industries Ltd. It was purified by passage through saturated aqueous potassium permanganate and then through concentrated sulphuric acid. Finally, it was triply distilled in vacuum, the first and last sixths of each fraction being discarded. The purity of chlorine prepared in this way is attested by other investigators (8, p. 253; 24).

Measurement of the Density of the Gas

Because of the reactivity of chlorine, the apparatus designed for this work was an all-glass system of the general type first used in this laboratory by Maass and Russell (15) and adapted, by Wright and Maass (25, 26), to the manipulation of gases that attack mercury. The latter investigators used a glass manometer in measuring the solubility of hydrogen sulphide in water and describe in detail the method of making the instrument (26). The glass manometer, calibrated volume, and condensation bulbs used in the density measurements proper were of Pyrex glass. Soft glass was used elsewhere for economy and also because soft glass stopcocks were more satisfactory with the lubricant used. The connections between Pyrex and soft glass were made with graded seals wherever chlorine was to be present and with deKhotinsky cement or solder seals in other parts of the system. Fig. 1 gives an outline of the cell, *V*, the glass manometer, *G*, and the

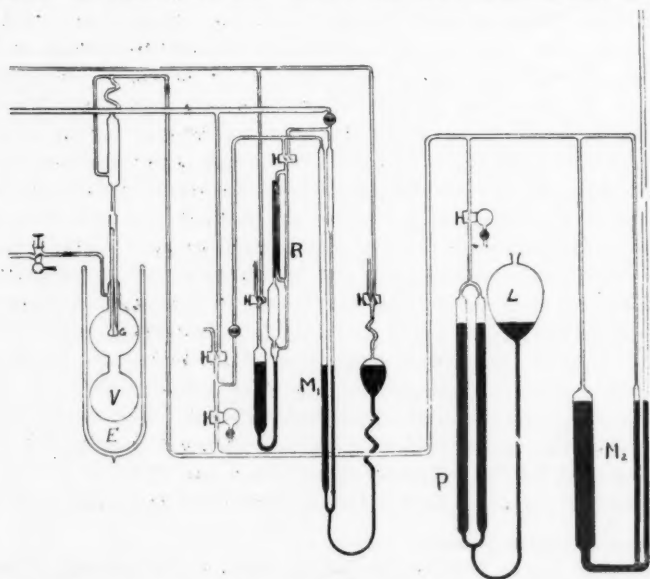


FIG. 1. Calibrated volume and manometers. *V*, calibrated volume; *G*, glass manometer; *M*₁, closed low pressure manometer; *M*₂, open high pressure manometer; *P*, *L*, pressure cylinders and levelling bulb; *R*, McLeod gauge.

associated parts of the system. In the work described here, the Dewar flask, *E*, was replaced with a large glass jar of about 25 litres capacity. Pressures were read either on the closed low pressure manometer, M_1 , or on the open high pressure manometer, M_2 , in which latter case the barometric pressure was added. Evacuation was checked with the McLeod gauge, *R*. Pressures greater than atmospheric were built up by compressing air in the cylinders, *P*, by raising the levelling bulb, *L*.

In view of the adequate information available in the literature on the general method involved in this investigation, emphasis may be laid on the special precautions required in the manipulation of chlorine. In all parts of the system that came into contact with chlorine, mercury-sealed vacuum stopcocks were necessary. The only satisfactory lubricant possessing the properties of non-reactivity and zero vapour pressure was the mixture of ortho- and meta-phosphoric acids described by Stephens (21). This lubricant is hygroscopic and must be protected from the water vapour in the atmosphere with a mercury seal. The application of vacuum to the base of the stopcock was desirable because it seated the plugs firmly in the barrels of the stopcocks and prevented channelling of the very viscous lubricant. Vacuum stopcocks were also required to take care of pressures greater than atmospheric in distillation and in the actual density measurements. It was found advisable to release the vacuum on the stopcocks whenever possible in order to prolong the life of the lubricating film. This precaution, desirable even with the best of organic lubricants when the stopcocks must be turned frequently, is imperative when inorganic lubricants of low lubricity must be used. A rough manometer containing mercury protected at its upper surface with a layer of Hyvac oil served to indicate the degree of vacuum applied to these stopcocks.

It was not possible to control the chlorine pressures at any point in the distillation system by means of a mercury manometer, because of the reaction between chlorine and mercury. The use of a manometric liquid such as concentrated sulphuric acid would have resulted in some solution of both chlorine and air, the latter being the chief impurity to be removed by the fractionation process, and the use of the complicated optical system and fragile glass manometer was not feasible. The rate of distillation was therefore controlled by keeping the chlorine below the ebullition point, by watching the rate of condensation of the chlorine in the receiver as indicated by the rate of evolution of carbon dioxide from the refrigerant surrounding it, and by observing the colour of the gas in the system, the depth of colour being a good measure of the concentration.

Special precautions had to be taken to prevent the diffusion of chlorine into the manometric system. Three sources of vacuum were used. Two of these were water aspirators. One was used for controlling the degree of vacuum on the pressure stopcocks lubricated with stopcock grease and the levelling devices on the low pressure manometer and the McLeod gauge. The other aspirator was used for removing chlorine from the system and for controlling the vacuum on the stopcocks lubricated with the phosphoric acid

mixture. Two mercury diffusion pumps in series, backed by a Hyvac pump, provided high vacuum whenever required. Air for flushing out the system was dried by passing it through two Drexel wash bottles in series, with concentrated sulphuric acid as the desiccant, and then over phosphorus pentoxide in a horizontal tube of 100 cm. length. Separate drying trains were provided for the air admitted to parts of the system containing chlorine and for the air admitted to the manometric system. Unless these precautions were observed the menisci in the manometers rapidly lost their sharpness of definition because of the formation of minute traces of mercurous chloride. Diffusion of water vapour from the aspirators to the system was prevented by the interposition of drying trains containing anhydrous calcium chloride on the aspirator side and phosphorus pentoxide next the system.

The cell used for the density measurements was calibrated *in situ* with gaseous sulphur dioxide, the density of which is accurately known, and also by expansion of air from another glass cell calibrated gravimetrically with water (3, p. 24). Concordant values were obtained by the two methods. Because of the reactivity of sulphur dioxide with the phosphoric acid lubricant, the density cell was connected, for calibration purposes, to a separate fractionation and condensation unit the stopcocks of which were lubricated with stopcock grease. The only stopcock common to both systems was the mercury seal vacuum stopcock attached to the cell. This stopcock was lubricated with grease for the calibration runs and afterwards cleaned with ether and lubricated with the phosphoric acid mixture when the cell was connected to the chlorine system. The sulphur dioxide was subjected to a triple fractionation *in vacuo* at low temperatures, as for the chlorine, and the volume of the cell calculated from the pressure-temperature-mass data and the apparent molecular weight of sulphur dioxide at the same temperature and pressure as given by the data of Cooper and Maass (1). With these values, the volume of the cell was obtained from the relation

$$\text{where} \quad V = \frac{w}{M'} \cdot \frac{RT}{P}$$

w is the weight of the gas condensed,

M' is the apparent molecular weight of sulphur dioxide at T and P ,

T is the temperature of the gas in $^{\circ}\text{K}.$,

P is the pressure in atmospheres, and

R is the gas constant in litre-atmospheres.

The volume of the cell at temperatures other than that of calibration was corrected for the thermal expansion of Pyrex balloons by applying the equation of Keyes (6),

$$V_t = V_0(1 + 9.68 \times 10^{-6}t + 3.11 \times 10^{-9}t^2),$$

where V_t is the desired volume at temperature t , and V_0 is the volume at $0^{\circ}\text{C}.$ The Keyes correction is just outside the experimental error. On the other hand, the Rayleigh correction, applied by Moles and Miravalles (19)

for differential pressure, is entirely negligible in this case compared to the errors incidental to the pressure measurements.

In both calibration and succeeding chlorine density measurements, the pressure was corrected for the residual pressure of gas remaining in the cell and connecting tubing after the condensation of the sample. These corrections were made in the usual way and all the customary precautions (14) were observed in weighing the bulbs containing the condensed gas samples.

The glass manometer in the cell was calibrated against the low pressure mercury manometer. The pointer sensitivity was 0.5 mm. of mercury per scale division, and the scale was read to 0.2 of a division. During actual pressure measurements the glass manometer was operated as nearly as possible as a null-point indicator so that the magnitude of the corrections for pointer displacement was small. The thermostat was a well lagged bath fitted with cooling coils and electric heaters. It was controlled by a thermoregulator to within 0.02° C. Temperatures were read on standard thermometers. All pressures were reduced to millimetres of mercury at 0° C. (7) and adjusted for slight deviations from the isothermal values by means of the relation

$$\frac{P_{\text{isothermal}}}{T_{\text{isothermal}}} = \frac{P_{\text{thermostat}}}{T_{\text{thermostat}}}$$

Results

The experimental data are given in Table I, where both densities and apparent molecular weights are listed. Fig. 2 shows the variation of the density of the gas with pressure.

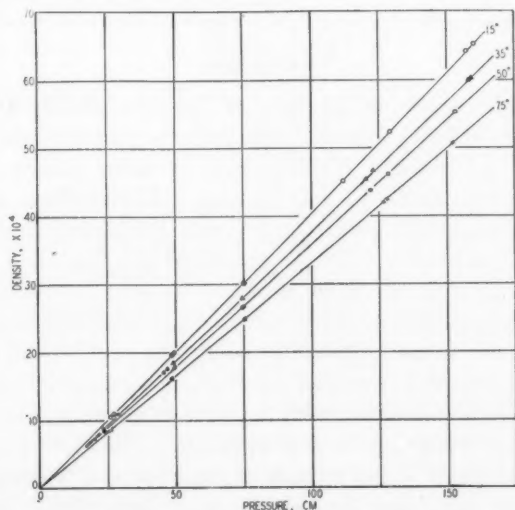


FIG. 2. Density of gaseous chlorine.

TABLE I
EXPERIMENTAL RESULTS

Pressure, mm. Hg	Absolute density, gm./cc.	M'	Pressure, mm. Hg	Absolute density, gm./cc.	M'
<i>Temp., 15.00° C.</i>			<i>Temp., 50.00° C.</i>		
261.9	0.001037	71.18	204.9	0.0007236	71.15
274.5	0.001089	71.26	238.2	0.0008410	71.15
490.4	0.001950	71.45	240.5	0.0008347	70.90
497.3	0.001980	71.56	495.8	0.001756	71.36
750.4	0.002998	71.80	498.6	0.001766	71.36
752.1	0.003003	71.76	747.0	0.002653	71.58
1120	0.004504	72.26	751.9	0.002673	71.63
1293	0.005217	72.49	1220	0.004361	72.04
1576	0.006396	72.92	1286	0.004598	72.03
1603	0.006508	72.97	1534	0.005509	72.36
<i>Temp., 35.00° C.</i>			<i>Temp., 75.00° C.</i>		
236.1	0.0008738	71.13	254.1	0.0008317	71.08
292.2	0.001084	71.30	254.6	0.0008324	70.98
458.3	0.001704	71.45	487.2	0.001601	71.35
470.6	0.001751	71.48	489.5	0.001606	71.25
492.9	0.001832	71.43	754.0	0.002480	71.40
748.5	0.002792	71.69	755.9	0.002486	71.39
750.9	0.002804	71.76	1269	0.004194	71.74
1205	0.004522	72.13	1280	0.004232	71.78
1234	0.004646	72.36	1525	0.005052	71.93
1585	0.005987	72.57			
1593	0.006014	72.54			

Discussion

In assessing the results in the light of the data already existing in the literature, it is of particular interest to compare them with the data of Jaquero and Tourpaian (4), who give 0.0028965 as the mean density, by their two methods, of chlorine at 15° C. and 725 mm. Interpolation of the present results gives a density of 0.002896 under these conditions, the deviation from Jaquero and Tourpaian's value being -0.04%. The data may also be compared directly with the value obtained by Pier at 50.24° C. and one atmosphere. Recalculation of this value to the isothermal temperature of 50.00° C. gives the value 0.002698 as compared to 0.002700 in this work. The deviation is +0.08% from Pier's value. It is also of interest to compare the results of this investigation with the data at temperatures and pressures outside the region of pressures and temperatures delineated by the isotherms at 15°, 35°, 50°, and 75° C. The data of Jaquero and Tourpaian at 0° and 725 mm. (0.9540 atm.) and the assortment of data offered by the work of Pier at higher temperatures and various pressures are available for this

purpose. The desired comparisons may be made by incorporating the results of this investigation in an equation of state and using the equation to calculate densities at the points where comparison is possible. Two such equations of state, both of which involve the variation of the viscosity of the gas with temperature, have been put forth by workers in this laboratory. The more precise of these equations is that of Cooper and Maass (2). This equation, however, involves a temperature function of such a nature that the constants of the equation can be evaluated only if highly accurate viscosity data are available. The equation of Maass and Mennie (14) involves Sutherland's equation (22) for the variation of viscosity with temperature which is known to be an approximation (23). Nevertheless, the accuracy of the density determinations in this investigation is such that the simpler equation of Maass and Mennie is quite adequate (25). Aberrations from the ideal gas law are most simply shown by tabulating the variation with temperature and pressure of the apparent molecular weight M' given by the relation

$$M' = \frac{wRT}{PV},$$

as has been done in Table I. If M_0 represents the theoretical molecular weight as given by the sum of the atomic weights involved, 70.91 in this case, then according to the equation of Maass and Mennie, the relation between M' and M_0 is given by

$$\frac{M'}{M_0} = 1 + \left(\frac{a - RTb}{R^2T^2} \right) P + 2 \left(\frac{a - RTb}{R^2T^2} \right)^2 P^2 + \dots$$

In this equation b is given by the relation

$$b = B \left(1 + \frac{c}{T} \right)$$

and B by the relation

$$B = \frac{8\sqrt{2}\pi r^3 N}{1 + \frac{c}{T}}$$

where r is the radius of the chlorine molecule, N is Avogadro's number, 6.062×10^{23} , and c is Sutherland's constant for the gas. From the values of r and c given by Jeans (5, pp. 288, 331)

$$B = \frac{8\sqrt{2}\pi(2.70 \times 10^{-8})^3 \times 6.062 \times 10^{23}}{1000 \left(1 + \frac{199}{273.2} \right)} = 0.2454.$$

The variation of b with temperature may then be calculated from the equation involving B , c , and T . To evaluate a , corresponding values of the molecular volume, temperature, and pressure were substituted in the approximate form of the van der Waals equation,

$$a = RT(V - b) - PV^2.$$

For the subsequent calculations the mean value of a , 16.93 over the temperature range 15° to 75° C. and at pressures of one and two atmospheres, was used.

Inasmuch as the theoretical density of a gas is given by the ideal gas law in the form

$$d_0 = \frac{PM_0}{1000RT},$$

where M_0 is the theoretical molecular weight of the gas, and the density under any actual conditions of temperature and pressure is given by the similar relation

$$d' = \frac{PM'}{1000RT},$$

where M' is the apparent molecular weight of the gas, it is evident that the equation of Maass and Mennie may be used to calculate densities in exactly the same way as it is used to calculate apparent molecular weights.

Written in this way the equation becomes

$$d' = \frac{PM_0}{1000RT} \left[1 + \left\{ \frac{16.93 - 0.2454RT \left(1 + \frac{199}{T} \right)}{R^2T^2} \right\} P + 2 \left\{ \frac{16.93 - 0.2454RT \left(1 + \frac{199}{T} \right)}{R^2T^2} \right\}^2 P^2 + \dots \right].$$

When the constants are collected this becomes

$$d' = \frac{0.86427P}{T} \left[1 + \left\{ \frac{2515 - 2.991(T + 199)}{T^2} \right\} P + 2 \left\{ \frac{2515 - 2.991(T + 199)}{T^2} \right\}^2 P^2 + \dots \right],$$

a convenient form for the calculation of the density of gaseous chlorine at any temperature and pressure within the range where the equation is valid.

In Table II, values of density and apparent molecular weight calculated with this equation are compared with corresponding values interpolated from the results of this investigation. The average deviation is $\pm 0.04\%$ and the net deviation given by the algebraic sum of the differences, calculated value less observed value, divided by the number of points at which comparison is made, in this case eight, is -0.01% .

Further evidence for the validity of this equation is given in Table III where calculated values of the density are compared with the data of Jaquero and Tourpaian and Pier. The agreement between the densities calculated with the aid of the equation and the densities observed by Jaquero and Tourpaian is striking. Their value at 15° and 0.9540 atm. (725 mm.) is the mean of a large number of measurements at temperatures and pressures close to the mean. As the density was determined by two different methods and with chlorine from three different sources, this mean value is undoubtedly the

TABLE II

ABSOLUTE DENSITY AND APPARENT MOLECULAR WEIGHT OF GASEOUS CHLORINE

Temp., °C.	Pressure in atmospheres							
	1		2		1		2	
	Absolute density, gm./cc.				Apparent molecular weight			
	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.
15.00	0.003038	0.003037	0.006159	0.006161	71.84	71.81	72.81	72.84
35.00	0.002834	0.002835	0.005731	0.005733	71.67	71.69	72.46	72.48
50.00	0.002699	0.002700	0.005450	0.005453	71.57	71.59	72.25	72.29
75.00	0.002500	0.002499	0.005039	0.005038	71.43	71.40	71.97	71.96

TABLE III

COMPARATIVE VALUES OF THE ABSOLUTE DENSITY OF GASEOUS CHLORINE AS DETERMINED BY VARIOUS WORKERS, WITH VALUES CALCULATED BY THE AUTHORS' EQUATION AFTER MAASS AND MENNIE

Temp., °C.	Pressure, atm.	Absolute density, gm./cc.		Investigator
		Calc.	Obs.	
0.00	1.0000	0.003212	0.003220	Pier (Moissan)
0.00	0.9540	0.003062	0.003063	Jaquerod and Tourpaian
0.00	0.1000	0.0003168	0.0003167	Pier
13.50	1.0000	0.003055	0.003058	Pier
13.50	0.4663	0.001414	0.001415	Pier
13.50	0.4201	0.001273	0.001274	Pier
13.50	0.2936	0.0008884	0.0008892	Pier
13.50	0.1951	0.0005896	0.0005899	Pier
13.50	0.1227	0.0003706	0.0003706	Pier
13.50	0.0569	0.0001717	0.0001717	Pier
15.00	0.9540	0.002896	0.002896	Jaquerod and Tourpaian
50.24	1.0000	0.002697	0.002696	Pier
99.95	0.1370	0.0003176	0.0003174	Pier
100.40	1.0000	0.002327	0.002324	Pier
100.40	1.3822	0.003224	0.003217	Pier
150.70	1.0000	0.002046	0.002044	Pier
184.00	1.0000	0.001896	0.001894	Pier
184.50	1.6960	0.003217	0.003215	Pier

most accurate yet established. The equation gives the same value. Jaquerod and Tourpaian made only one determination at 0° and this was also at 725 mm. pressure, but it was made with great care. The difference, density calculated less density observed, in this case is only -0.036%. When the calculated values are compared with the data of Pier, the agreement between the calculated and observed values is very good at all pressures below 0.2 atm. and satisfactory at the higher pressures. Deviations significantly larger than average occur at 0° and 1 atm. and at 100.4° and 1.3822 atm. Pier's value at 0° and 1 atm. is based on Moissan's absolute measurements (16, 17, 18), and all his measurements are relative to these, depending on the analytical deter-

mination of the quantity of chlorine in a known volume referred to Moissan's value as a measure of the purity of the gas which he used. Moissan's value, 2.490, for the relative density of chlorine with respect to air at 0° and 1 atm., when converted to absolute density is 0.0032196, and this is 0.19% higher than the best value (3), 0.003214, calculated by Jaquerod and Tourpaian. However, as Jaquerod and Tourpaian depended in part upon the data of Leduc (9-13), whose relative value is 2.491 as compared to Moissan's 2.490, it is evident that both the calculations of Jaquerod and Tourpaian and, to a considerably greater extent, those of Pier, are based upon values that are too high. Since Pier calculated all quantities of chlorine found analytically from a supposed purity of 99.32% to a 100% basis, his values may be expected to be considerably higher than the true values. This is evident in his values at 0° and at 13.5°. The deviation which reaches a maximum in the opposite direction at 100.40° and 1.3822 atm. is clearly attributable to experimental error since a plot of Pier's relative densities against temperature shows in this region a marked change of slope which cannot be predicted on theoretical grounds or by analogy with similar gases. Pier's assumption of dissociation is contradicted by the insignificant degree of dissociation found at much higher temperatures and also by the fact that his values again approach, at higher temperatures, the values predicted by the equation. In view of the fact that Pier's values deviate in opposite directions over the range investigated by him, the net deviation as defined above is fortuitously good, being + 0.003%. The average deviation, however, is much larger than in the present investigation and amounts to $\pm 0.86\%$.

It will be seen that the absolute values obtained in this investigation are in best agreement with those of Jaquerod and Tourpaian at 0° and 15° and at a pressure of 725 mm. Furthermore, the equation relating density to temperature and pressure is shown to be in agreement with the experimental results to an average of 1 part in 2500 over the whole pressure-temperature range investigated. The pressure-density variation determined by Pier at 13.5° and at pressures from 0.0569 to 1 atm. agrees with the equation based on the experimental findings of this work to an average of 1 part in 1700. In addition, there is agreement to an average of 1 part in 1200 between the calculated values and the densities determined by Pier at temperatures up to more than 100° above the upper temperature limit of this work and at pressures as high as 1.696 atm. As far as the standard value of the density of chlorine at 0° and 1 atm. is concerned, the value calculated by means of the equation agrees to 1 part in 1600 with the standard value (3, p. 3) of Jaquerod and Tourpaian. However, in the light of the above discussion the standard value calculated by means of the equation is possibly more accurate than the value hitherto accepted.

To sum up, the equation of state herein described appears to represent the density of gaseous chlorine with an accuracy of 1 part in 5000 when compared with the basic data of Jaquerod and Tourpaian at 15° and 725 mm. Its agreement to 1 part in 2000 or better with the results of this investigation

and good agreement with the scattered data of Pier at higher temperatures indicate that it may be safely used to calculate the density of the gas over the range 0° to 200° C. and at pressures up to about five atmospheres.

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SOLID SOLUTIONS OF HYDROGEN PEROXIDE AND WATER¹

BY P. A. GIGUÈRE² AND O. MAASS³

Abstract

An attempt has been made to determine the exact composition of the first crystals that separate out on freezing solutions of hydrogen peroxide and water of various concentrations. Special care was taken to ensure complete removal of any liquid wetting the solid phase. In all cases the crystals were found to contain both components and in proportions usually different from those in the mother-liquor. Owing to the limitations of the experimental method used, the results are only approximate, but they afford ample evidence for the existence of solid solutions. The possibility of hydrogen peroxide forming solid solutions with water is discussed from the standpoint of the crystal structure of both components.

Introduction

Following a program of research carried out in this laboratory for the purpose of determining the physical and chemical properties of hydrogen peroxide, it was found advisable to systematize the preparation of this compound in the pure state. The method originated by Maass and Hatcher (8) consisted first in purifying a 30% commercial solution of hydrogen peroxide in water by distillation under reduced pressure in an all-glass apparatus. This pure solution was then concentrated to over 90% by fractional distillation in a similar apparatus. In connection with these two stages of the process, the total and partial vapour pressures of binary solutions of hydrogen peroxide and water have been measured at three different temperatures over the whole concentration range (5). The latter investigation, which is to be described in a subsequent paper, has proved that the only practicable method for obtaining 100% pure hydrogen peroxide is by fractional crystallization of its concentrated solutions. In the present case, the efficiency of a fractional crystallization depends upon the phase equilibrium in the two component system: water-hydrogen-peroxide. The freezing-point curve of this system was determined for the first time by Maass and Herzberg (9). However these authors made no attempt to determine the composition of the crystals that separated out at various concentrations, so that their results were sometimes interpreted as disproving the existence of solid solutions (3). If such were the case, pure hydrogen peroxide could easily be prepared from solutions containing over 60% peroxide, as may be seen from the freezing-point diagram. Actually such a conclusion is in disagreement with current experience. Indeed a number of observations recorded in this laboratory have shown that, in spite of all the precautions taken to secure a complete separation of the two

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phases, the effective concentration in one operation was usually around 2% and never greater than 4%. It was therefore not deemed expedient to attempt the preparation of anhydrous hydrogen peroxide from solutions of any concentration below 90%.

From the theoretical point of view, hardly any prediction could be made. The few experimental data available on this subject have not so far permitted a rigorous definition of the conditions requisite for the formation of solid solutions.

Experimental

The composition of the solid phase was determined directly; that is, the crystals were filtered from the partially frozen solution and were analysed after removal of the absorbed mother-liquor. The last operation was obviously of great importance for obtaining reliable results. In this connection, the low temperature at which the separation had to be carried out in many cases, and, furthermore, the very fine structure of the solid phase itself, presented many experimental difficulties. After a number of unsuccessful attempts the following technique was adopted.

The solution, about 100 cc. contained in a large Pyrex test tube, was cooled down to a few degrees below its freezing point in an appropriate freezing mixture. To overcome the supercooling that invariably takes place, the test tube had to be brought into contact with some cold material, dry ice or even liquid air in some cases, until a few crystals appeared. While solidification was taking place, the solution was stirred mechanically and the temperature of the cooling bath was kept constant to within $\pm 2^\circ$. Usually after 15 min. about one-fifth of the solution was crystallized. The separation of the two phases was then effected by means of the apparatus illustrated in Fig. 1. The mixture was poured quickly into tube A, which was also kept in the cooling

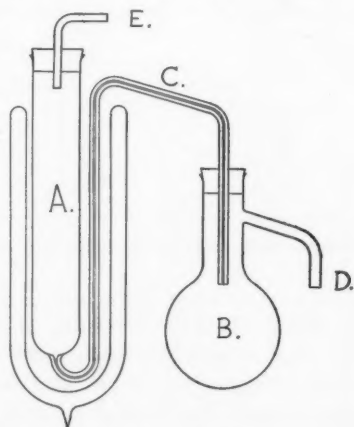


FIG. 1. Diagram of apparatus used for separating the crystals from the solutions of hydrogen peroxide.

bath. From there, the liquid was siphoned into flask *B* through the capillary tube *C* by applying a slight suction at *D*. This operation had to be handled so as to avoid stopping up the capillary tube. The liquid phase was then contained in *B*, and the solid phase, still wetted by the liquid, was left behind in *A*. To dry it as completely as possible, suction was applied continuously at *D* for at least 15 min. The air entering at *E* was previously cooled and carefully dried over sulphuric acid and phosphorus pentoxide. Finally, to remove the last trace of adhering mother-liquor, the temperature of the cooling bath surrounding *A* was allowed to rise slowly until the crystals just started to melt. The resulting liquid was carried into flask *B* by suction. The composition of both phases was determined by titration against standard potassium permanganate.

Results

The freezing-point curve of solutions of hydrogen peroxide and water has been redetermined at some thirty different concentrations, this time by means of a calibrated toluene thermometer. The results are given in Table I, and plotted in Fig. 2, line *A, B, C, D, E*. The co-ordinates of point

TABLE I
FREEZING POINT OF SOLUTIONS OF HYDROGEN AND WATER

H ₂ O ₂ , %	Freezing point, °C.	H ₂ O ₂ , %	Freezing point, °C.
4.5	- 2.2	27.7	-22.2
8.1	- 4.4	30.0	-25.1
9.9	- 6.1	31.4	-27.4
14.5	- 9.2	33.8	-30.3
17.6	-11.7	36.6	-33.5
22.2	-16.2	42.0	-44.5
24.0	-18.5	44.7	-50.8
46.0	-51.1	54.0	-51.5
48.0	-50.2	56.3	-52.2
51.1	-50.5	58.2	-53.6
60.2	-54.0	78.2	-26.3
63.5	-50.0	80.5	-22.2
68.0	-43.5	85.3	-17.4
70.1	-39.7	90.1	-11.2
76.0	-30.4	100.0	-0.89*

* From the very careful determination made by Maass, Cuthbertson, and Matheson (10).

C are: -50.3°, 48.6%, the latter value being obtained from the composition of the hydrate: H₂O₂ · 2H₂O. The temperatures of the two eutectics: *B*, -51.5° and *D*, -56.5°, were obtained by extrapolation of the three sections of the curve. The results corresponding to the solid solutions are presented in Table II. The composition of the original solution used in each case, as well as that of the two phases which were obtained from it, are expressed in terms of hydrogen peroxide in percentage by weight. The temperature at

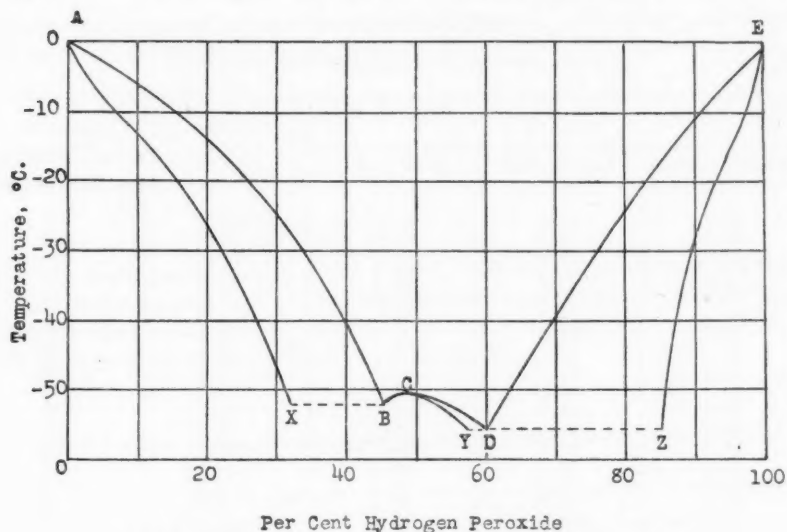


FIG. 2. Phase rule diagram of the system water-hydrogen-peroxide.

which the crystallization was carried out is also recorded, together with that corresponding to the freezing point of the liquid phase. This last value, when plotted against the composition of the corresponding solid phase, gives the so-called "solidus", or melting-point curve, line A, X, Y, Z, E, in Fig. 2, of the system, water-hydrogen-peroxide.

TABLE II
SOLID SOLUTIONS OF HYDROGEN PEROXIDE AND WATER

Original solution	H ₂ O ₂ , %		Melting point, °C.	Temp. of freezing, °C.
	Liquid phase	Solid phase		
8.2	9.6	1.7	-5.5	-8
10.9	12.5	2.6	-7.5	-10
20.5	21.2	14.5	-16.0	-20
21.5	23.2	15.0	-17.5	-22
31.4	32.3	20.0	-27.2	-32
31.4	33.5	20.8	-27.9	-34
31.4	32.8	20.4	-28.1	-34
39.2	40.8	28.2	-41.6	-44
39.4	41.0	29.6	-41.7	-45
46.2	46.1	46.8	-51.5	-58
48.5	48.5	48.4	-50.1	-54
48.6	48.5	48.7	-50.1	-56
56.5	56.2	53.5	-52.4	-60
65.3	63.2	87.5	-51.0	-56
69.6	67.5	86.5	-44.2	-50
70.7	68.0	87.6	-43.0	-50
71.0	69.7	86.0	-40.1	-46
71.8	70.2	86.1	-39.6	-46

TABLE II—*Concluded*

SOLID SOLUTIONS OF HYDROGEN PEROXIDE AND WATER

Original solution	H ₂ O ₂ , %		Melting point, °C.	Temp. of freezing, °C.
	Liquid phase	Solid phase		
72.2	71.0	87.5	-38.5	-43
74.0	72.5	86.0	-36.0	-40
79.5	75.6	89.2	-31.3	-36
77.2	76.3	89.5	-29.4	-32
78.8	77.5	92.0	-28.1	-32
81.5	79.5	92.6	-24.5	-30
82.5	81.5	93.0	-21.6	-26
82.5	81.7	91.5	-21.0	-26
83.5	83.3	92.7	-19.1	-24
85.3	83.3	94.5	-19.1	-25
86.0	84.0	92.6	-18.2	-23
86.8	86.5	95.0	-15.0	-21
89.0	87.6	94.5	-13.7	-20
93.5	93.0	98.1	-7.5	-14
96.0	93.2	98.5	-7.2	-12
94.0	93.3	98.2	-7.0	-9
94.5	94.5	98.6	-6.3	-10
96.1	95.5	98.8	-5.0	-9

Discussion

The conspicuous fact in the above results is the existence of solid solutions of hydrogen peroxide and water. It is significant that in no instance was it possible to obtain either pure ice or pure hydrogen peroxide crystals from solutions containing more than 2 or 3% of the other component. This fully confirms the observations previously recorded by other investigators. The absorption phenomena alone could not possibly be the cause of this state of affairs. Indeed, a simple calculation shows that the solid phase should have contained as much as 50% of the mother-liquor; this is rather unlikely in view of the extra precautions actually taken. In agreement with the phase rule, the two phases in equilibrium at point C were found to have the same composition.

As a whole, the results are fairly consistent, although no great accuracy can be claimed for any one in particular. On the other hand, it is felt that the possibilities of the analytical method have been used to the limit in the present investigation. The indirect method, which Bancroft (1) described under the title of "Synthetic Analysis of the Solid Phase", obviates the tedious and problematic separation of the solid phase. Unfortunately the instability of hydrogen peroxide and the fact that it forms addition compounds with many salts made this method unsuited to the present case.

The formation of solid solutions, and the existence of a definite compound, are two factors that cause the freezing-point curve of solutions of hydrogen peroxide and water to deviate from that of an ideal solution. A quantitative measure of the aberration from Raoult's law can be obtained (4) by com-

paring the observed values of the freezing-point with those calculated* by means of the well-known equation:

$$\frac{dx}{dT} = \frac{L}{RT^2},$$

or better, since the above equation holds only for very dilute solutions, by the following:

$$\ln(x) = \frac{-L}{R} \left(\frac{1}{T_1} - \frac{1}{T_0} \right),$$

where x is the mole fraction of the solvent, L is its molecular heat of fusion, T_0 its melting point, and T_1 the equilibrium temperature in absolute units, R is the gas constant in heat units. The two sets of values for each side of the freezing-point diagram are given in Table III.

TABLE III

CALCULATED AND OBSERVED VALUES FOR THE FREEZING POINT OF SOLUTIONS OF WATER AND HYDROGEN PEROXIDE

Water side			Hydrogen peroxide side		
H ₂ O ₂ , %	Freezing point		H ₂ O %	Freezing point	
	Obs.	Calc.		Obs.	Calc.
1	-0.6	-0.56	1	-1.7	-2.01
2	-1.2	-1.11	2	-2.4	-3.09
4	-2.3	-2.24	4	-4.4	-5.24
6	-3.5	-3.38	6	-6.4	-7.37
8	-4.8	-4.57	8	-8.4	-9.51

The discrepancy found between the experimental and the calculated values in the case of solutions of high peroxide content may be ascribed to the influence of solid solutions. Lewis and Randall (7) have given the following equation† in which the lowering of the freezing point is related to the distribution coefficient K of the solute between the solid and the liquid phases:

$$\frac{dT}{dx} = (K - 1) \frac{RT^2}{L}$$

By means of this equation, a corrected value for the freezing point of these solutions was derived. Conversely, from the observed freezing point, the composition of the solid phase was calculated. These results are contained in Table IV.

Inspection of Table III shows that the above speculations do not apply to dilute solutions of hydrogen peroxide since their freezing-point curve agrees closely with that of an ideal solution for concentrations up to 6%. Truly

* Taking the value of 74.1 for the latent heat of fusion of hydrogen peroxide (8), the molecular depression of the freezing point in this solvent is found to be 1.98 as compared with 1.86 in water.

† For ideal solutions.

TABLE IV
FREEZING POINTS CORRECTED FOR THE INFLUENCE OF SOLID SOLUTIONS

H ₂ O in liquid phase, %	Freezing point		H ₂ O in solid phase, %	
	Obs.	Corr.	Obs.	Calc.
1	-1.7	-1.71	0.28	0.25
2	-2.4	-2.48	0.55	0.45
4	-4.4	-4.25	0.91	0.86
6	-6.4	-5.83	1.43	1.46
8	-8.5	-7.16	2.24	2.17

enough, the formation of a compound tends to lower the freezing-point curve, but that influence is rather unimportant at such low concentrations.

Until a few years ago, virtually nothing was known of the crystal structure of hydrogen peroxide. The X-ray diffraction investigations of Fehér and Klötzer (2, 3) have recently established that hydrogen peroxide has a tetragonal symmetry. For comparison, their numerical results are summed up in Table V, along with the corresponding values for ice. These results were confirmed independently by Natta and Rigamonti (11). Furthermore, these authors, using concentrated solutions of hydrogen peroxide instead of the pure compound, arrived at the conclusion that hydrogen peroxide does not take either water or the dihydrate into solid solutions. Their conclusion was based on the fact that the diffraction patterns of 82% and 90% solutions showed identical intensities and lattice constants for hydrogen peroxide. Many examples are known however of non-isomorphous compounds forming solid solutions (12). Although water and hydrogen peroxide do not crystallize in the same system, the two lattices are fairly simple, and their cell volumes are not so dissimilar as to exclude the possibility of their sharing a common structure.

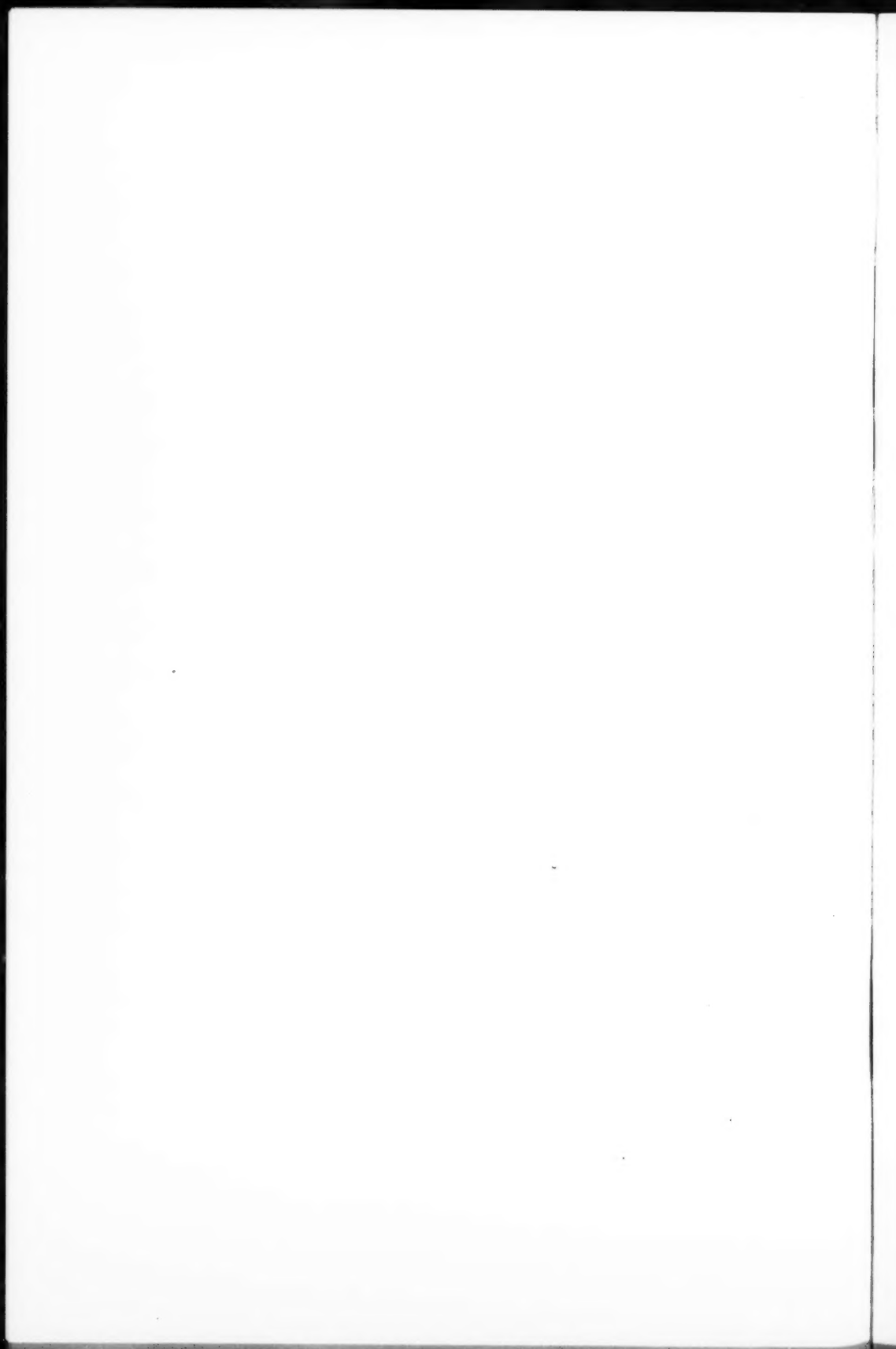
TABLE V
COMPARISON OF CRYSTAL STRUCTURE OF ICE AND SOLID HYDROGEN PEROXIDE

Substance	System	Axes (Å)		Volume of cell, Å ³	Space group	Molecules per unit cell
		<i>a</i>	<i>c</i>			
H ₂ O	Hexagonal	4.53	7.41	132	<i>D</i> ₄	4
H ₂ O ₂	Tetragonal	4.02	8.02	128	<i>D</i> ₂ ^h or <i>D</i> ₂ ^d	4 (?)

In view of the importance of this problem, it seems desirable that it should be thoroughly investigated by means of X-ray diffraction methods. Apart from the theoretical interest attached to the results obtained, this investigation has contributed much useful information regarding the preparation of pure hydrogen peroxide.

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